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Impact of NOx Selective Catalytic Reduction Processes on Flue Gas Cleaning Systems

Radian Corp.
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Prepared for

Industrial Environmental Research Lab.
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IMPACT OF NO_X
SELECTIVE CATALYTIC REDUCTION
PROCESSES ON FLUE GAS
CLEANING SYSTEMS

Prepared for

Office of Environmental Engineering and Technology

Prepared by

Industrial Environmental Research
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16. ABSTRACT The report gives results of a study of the impact of the ammonia leaving a nitrogen oxide (NOx) selective catalytic reduction (SCR) process on downstream flue gas cleaning processes. (NOx emissions from electric utility boilers may be reduced 80-90% by the application of pollution control technology based on the SCR of NOx with ammonia; however, some unreacted ammonia may be emitted from the control system.) These processes include electrostatic precipitators (ESPs), baghouses, and flue gas desulfurization (FGD) systems. In normal operation, most ammonia leaving the SCR system will be removed, either as particulate salts by the particulate removal system or as free ammonia by the FGD system. Very little ammonia should be emitted at the stack. The operation of ESPs and FGD systems will, in most cases, be improved by the presence of ammonia in the flue gas. The effects of ammonia and ammonia salts on baghouse operation are not known. At normally expected emission levels, no adverse environmental impacts are projected; however, at high ammonia emission levels, the potential exists for problems with ammonia in the waste streams from fly ash and SO2 collection devices. Potential adverse environmental impacts exist in the ash and sludge ponds where collected ammonia may be concentrated and emitted as a gaseous pollutant.

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April 1982

IMPACT OF NO_x SELECTIVE CATALYTIC REDUCTION PROCESSES ON FLUE GAS CLEANING SYSTEMS

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ABSTRACT

Nitrogen oxide (NO_x) emissions from electric utility boilers may be reduced by 80-90% through the application of pollution control technology based on the selective catalytic reduction (SCR) of NO_x with ammonia (NH_3); however, some unreacted ammonia may be emitted from the control system. This study was performed to investigate the impact of the ammonia leaving a NO_x SCR process on downstream flue gas cleaning processes. These include electrostatic precipitators (ESP), baghouses, and flue gas desulfurization (FGD) systems. Under normal operating conditions, most of the ammonia leaving the SCR system will be removed, either as particulate salts by the particulate removal system or as free ammonia by the FGD system. Very little ammonia should be emitted at the stack. The operation of ESP and FGD systems will, in most cases, be improved by the presence of ammonia in the flue gas. The effects of ammonia and ammonia salts on baghouse operation are not known; however, if the compounds formed are sticky, adverse effects may occur. At normally expected emission levels, no adverse environmental impacts are projected; however, at high NH_3 emission levels, the potential exists for problems with NH_3 in the waste streams from fly ash and SO_2 collection devices. Potential adverse environmental impacts exist in the ash and sludge ponds where collected ammonia may be concentrated and emitted as a gaseous pollutant.

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SECTION 1

SUMMARY

Selective catalytic reduction (SCR) systems in Japan have achieved 80-90 percent NO_x reductions on gas and oil-fired utility boilers. Commercial demonstrations of this technology on a coal-fired boiler are underway in Japan.[1] It is expected that 80-90 percent NO_x reductions will result in 10-20 ppm of ammonia existing in the gas exiting the SCR. The effect of this ammonia on downstream equipment is summarized below.

1.1 AMMONIA REMOVAL BY DOWNSTREAM EQUIPMENT

The results of a comparison study on the formation of ammonia salts indicate that downstream of the air preheater, ammonia (NH_3) will react with sulfur trioxide and hydrogen chloride (HCl) to form particulates. The reactions, in order of occurrence are:

$$NH_3 + SO_3 + H_2O \rightleftarrows NH_4HSO_4\,(\ell) \qquad (1\text{-}1)$$

$$NH_3 + NH_4HSO_4 \rightleftarrows (NH_4)_2SO_4\,(s) \qquad (1\text{-}2)$$

$$NH_3 + HCl \rightleftarrows NH_4Cl\,(s) \qquad (1\text{-}3)$$

A literature search concerning ammonia injection for improved ESP performance indicated that, under normal operating conditions, the ESP would remove approximately 90% of these particulate salts. Ammonia removal by the ESP will only occur to the extent that the ammonia reacts with SO_3 and HCl. Unreacted ammonia will remain in the gas phase and pass through the ESP.

A baghouse is more efficient than an ESP in collecting fine particles and, consequently, the predicted removal of ammonia salts by a baghouse is 99%. As with the ESP, unreacted ammonia will not be collected by a baghouse.

The level of ammonia removal which will occur in FGD systems depends on the form of the ammonia in the flue gas, the pH of the FGD system scrubbing liquor, and the type of contactor used in the FGD.

Computer simulations were run at steady state ammonia concentrations of the scrubber inlet of 0,10,20,50 and 100 ppm at the inlet of a limestone scrubber for both Eastern and Western coal. The ammonia removal in each case is shown in Table 1-1.

TABLE 1-1. AMMONIA REMOVAL BY FGD SCRUBBER AS A FUNCTION OF COAL TYPE AND AMMONIA CONCENTRATION

Case	NH_3 in Scrubber Inlet Gas, ppm	Eastern Coal		Western Coal	
		pH	NH_3 removal, %	pH	NH_3 removal, %
1	100	6.0	85	6.2	25
2	50	5.9	90	6.0	35
3	20	5.9	93	5.9	45
4	10	5.9	95	5.9	55
5	0	5.9	100	5.8	100

For limestone scrubbing systems (with particulate removal upstream), about 50 percent of the gaseous ammonia will be removed in a Western coal application and about 95 percent of the gaseous ammonia will be removed in an Eastern coal application for ammonia concentrations of 10-20 ppm entering the FGD system. At the lower ammonia concentrations (1-3 ppm) normally expected at the FGD inlet, higher percentage removals are expected. Removals for the Western coal case are lower since the coal has a lower sulfur content. Low sulfur coals result in lower blowdown rates and higher liquid ammonia concentrations in the scrubbing liquor thereby reducing the concentration driving force for $NH_3(g)$

removal. Assuming a system is not mass transfer area limited, the $NH_3(g)$ removal is proportional to the difference in the gas phase and liquid phase concentrations. Other FGD systems which typically operate at higher pH levels should not achieve gaseous ammonia removals as high as limestone FGD systems.

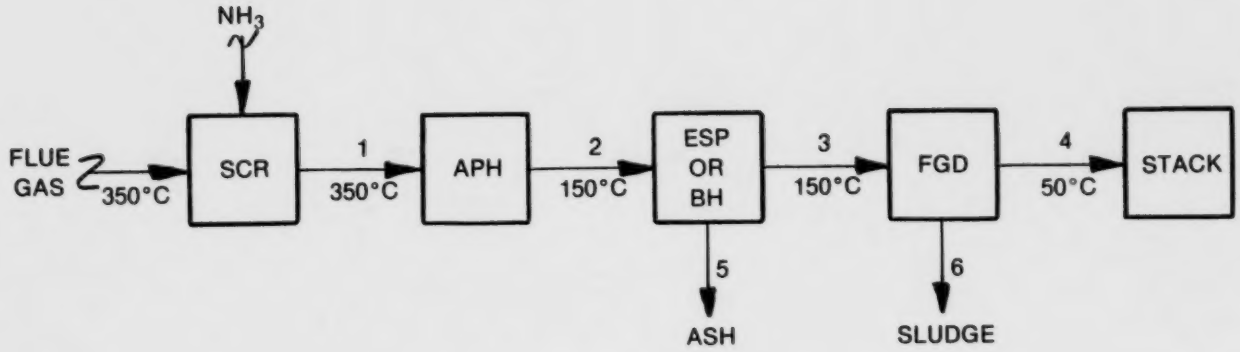
The amount of ammonia salts in the flue gas which will be removed in an FGD system will depend on the type of contactor used. A low pressure drop contactor such as a spray tower (commonly used in limestone FGD systems) should not remove a significant portion since these salts are typically submicron in size. Higher pressure drop contactors such as packed or mobile bed types may achieve greater removal of the submicron ammonia salt particulate from the flue gas. However, for the typical configuration, most of the ammonia salts would be removed in an upstream ESP or baghouse.

The ammonia removal by a dry FGD system is not known. However, ammonia salts formed as the flue gas coals will be collected by the baghouse downstream of the FGD system.

To summarize, ammonia exiting the SCR reactor can be partially removed by downstream equipment by two mechanisms: (1) reaction with SO_3 or HCl to form particulates which are partially removed by the ESP or baghouse, and (2) absorption of free ammonia into the FGD scrubbing liquor. It is not possible to make a general prediction of the magnitude of ammonia removal by these mechanisms since ammonia removal is affected by the concentrations of several flue gas components, especially SO_2, SO_3 and HCl. Some hypothetical examples of ammonia removal are illustrated in the following discussion.

1.2 ULTIMATE FATE OF AMMONIA

NH_3 removal by flue gas treating equipment is illustrated in Figures 1-1 through 1-3 where three cases are considered, these being:



NH_3 IN SCR EXIT GAS	10 ppm						50 ppm						100 ppm					
STREAM	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
NH_3	10	1	1	0	0	0	50	4	4	0	0	0	100	8	8	2	0	0
SO_3	30	21	21	21	0	0	30	0	0	0	0	0	30	0	0	0	0	0
HCL	70	70	70	7	0	68	70	70	70	7	0	59	70	38	38	4	0	26
NH_4HSO_4	0	9	1	1	8	0	0	30	2	2	28	0	0	0	0	0	0	0
$(NH_4)_2SO_4$	0	0	0	0	0	0	0	7.5	1	1	6.5	0	0	30	2	2	28	0
NH_4CL	0	0	0	0.2	0	1	0	1	1	2	0	4	0	32	2	4	30	6

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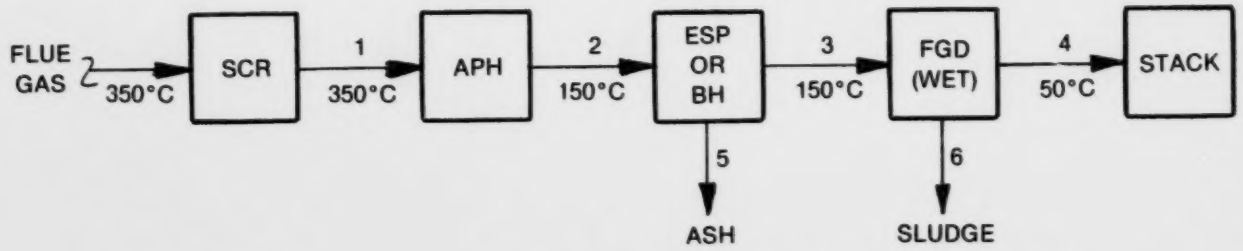
Figure 1-1. Fate of NH_3, SO_3 and HCl in Flue Gas Cleaning System Eastern coal, wet FGD. (All concentrations expressed in ppmv equivalents).



NH_3 IN SCR EXIT GAS	10 ppm						50 ppm						100 ppm					
STREAM	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
NH_3	10	2	2	2	0	0	50	28	28	15	0	0	100	71	71	64	0	0
SO_3	4	0	0	0	0	0	4	0	0	0	0	0	4	0	0	0	0	0
HCL	25	25	25	3	0	20	25	11	11	1	0	8	25	4	4	0	0	1
NH_4HSO_4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$(NH_4)_2SO_4$	0	4	0.2	0.2	3.8	0	0	4	0.2	0.2	3.8	0	0	4	0.2	0.2	3.8	0
NH_4CL	0	0	0	0	0	2	0	14	1	12	13	2	0	21	1	5	20	3

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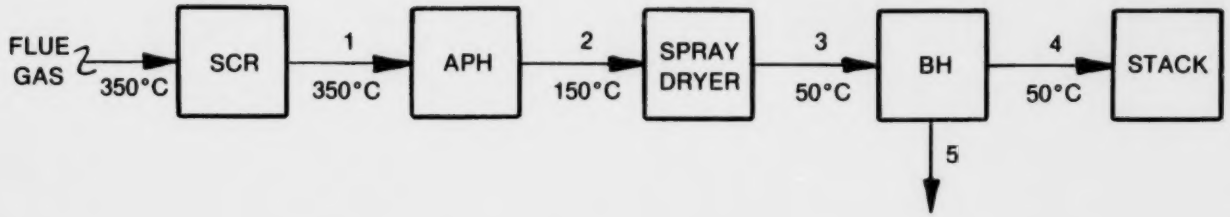
Figure 1-2. Fate of NH_3, SO_3 and HCl in Flue Gas Cleaning System Western coal, wet FGD. (All concentrations expressed in ppmv equivalents).



NH_3 IN SCR EXIT GAS	10 ppm					50 ppm					100 ppm				
STREAM	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
NH_3	10	2	0	0	0	50	28	17	?	?	100	71	67	?	?
SO_3	4	0	0	0	0	4	0	0	0	0	4	0	0	0	0
HCL	25	25	23	2	21	25	11	0	0	0	25	4	0	0	0
NH_4HSO_4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$(NH_4)_2SO_4$	0	4	4	0	4	0	4	4	0	4	0	4	4	0	4
NH_4CL	0	0	2	0	2	0	14	25	0	25	0	21	25	0	25

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Figure 1-3. Fate of NH_3, SO_3 and HCl in Flue Gas Cleaning System Western coal, dry FGD. (All concentrations expressed in ppmv equivalents).

1) Eastern coal, wet FGD,

2) Western coal, wet FGD, and

3) Western coal, dry FGD.

In each case three levels of NH_3 emissions from the SCR system are presented. Ten ppm is considered to be a normal emission level, 50 ppm is a high level and 100 ppm which is significantly higher than would be anticipated. The material balances presented in the figures are calculated values based on a number of assumptions.

In the first case, Eastern coal with wet FGD, no NH_3 is emitted at the stack due to the large concentrations of SO_3 and HCl present. The bulk of the NH_3 is removed as salts in the ESP or baghouse and small quantities are removed in the scrubber. This is not the case with Western coal (Figure 1-2) since SO_3 and HCl concentrations are substantially lower. With Western coal, the NH_3 reacts completely with SO_3 and to equilibrium with HCl. Some, but not much of the remaining free NH_3 is removed by the scrubber. Even with 50 ppm of NH_3 in the SCR exit gas, the stack concentration is only 15 ppm which is acceptably low. The stack gas will also contain the equivalent of 12 ppm of NH_4Cl as a particulate. With Western coal and a spray dryer the amount of NH_3 in the stack gas will not change, but the amount of particulates will be significantly reduced by the downstream baghouse.

The results of these material balances indicate that ammonia emissions will not be a problem, even at SCR reactor outlet concentrations of up to 50 ppm, when the SCR system is followed by a particulate collection device and an FGD system. Ammonia emissions will be significantly reduced by this downstream equipment when high sulfur Eastern coal is used. The ammonia that is removed by downstream equipment ultimately ends up in the waste streams from these processes and it is these streams which have a potential for environmental impact.

1.3 IMPACTS OF AMMONIA ON DOWNSTREAM EQUIPMENT

Ammonia in the flue gas can impact downstream equipment in two ways: by affecting the performance and/or the waste stream. These impacts were examined by both literature survey and original analysis.

1.3.1 Operational Impacts

Ammonia injection upstream of ESP's is a common practice at some plants and, in the older units, high ammonia levels (<50 ppm NH_3) have caused excessive fly ash adhesion. This operational problem may be overcome by increasing rapping frequency and/or intensity, or by periodic washing of the ESP collector plates. Baghouse operation may be impaired due to the presence of ammonium bisulfate, which is liquid at 147°C, and may cause blinding of the filter bags. More frequent cleaning and bag replacement may be required; however, investigations are needed to assess the severity of this problem since no commercial experience is available for study.

One alternate equipment configuration is the use of a hot-side ESP. As stated earlier, the operating temperature upstream of the air preheater is about 100°C higher than the formation temperature of the ammonia salts. Consequently, very little ammonia salt removal would occur if the hot side ESP was downstream of the SCR. Obviously, no ammonia salt removal would occur with the ESP upstream of the SCR. This configuration has been proposed for use in Japan to prevent contamination of the ash with the ammonia salts. However, in this configuration, it is probable that control of the submicron ammonia salts will be difficult. Low pressure drop SO_2 scrubbers will not remove these fine particulates and it is possible that this configuration could result in a visible plume unless additional particulate control devices are employed.

A fabric filter following a spray dryer FGD system should remove most of the ammonium salt particulates. Since ammonium bisulfate is not liquid at these temperatures (~65-95°C) the potential for filter media blinding is reduced.

With respect to FGD systems, the presence of ammonia in the scrubbing liquor will be beneficial with respect to SO_2 removal. At expected FGD inlet NH_3 levels of 1-2 ppm, a slight rise in the SO_2 removal efficiency may be observed. At higher levels (10-20 ppm inlet to FGD), the L/G ratio could be reduced while maintaining a constant 90 percent SO_2 removal. At very high levels (>50 ppm) of gaseous ammonia entering the FGD system, substantial improvements in the SO_2 removal would occur. However, evolution of ammonia may also occur over tanks, filters and other open vessels causing some operator complaints.

Other types of wet FGD systems should exhibit slightly increased SO_2 removal because of ammonia in the gas. Spray dryers will probably not remove significant amounts of gaseous ammonia; however, the baghouse should collect essentially all of the ammonia salts. Regenerable FGD systems may require additional equipment to remove ammonia from the byproduct stream.

1.3.2 Waste Stream Impacts

Handling of the fly ash containing ammonium sulfate salts can potentially cause ammonia emissions. The vapor pressure of ammonia over the solid salts is very low, but, if the ash is wetted or sluiced, gaseous ammonia will evolve. The phenomena is dependent on the pH and ammonia concentration of the liquid. Sluicing of the ash will dissolve the ammonia salts and could lead to aqueous ammonia discharges if the sluice water is not recycled. Ten ppm of ammonia in the SCR exit gas could result in ammonia concentrations in the ash pond overflow of 30 mg/ℓ for Eastern coal and 60 mg/ℓ for Western coal.

The potential also exists for ammonia to leach into the ground water from the fly ash pond. With proper pond lining, however, the probability of this occurring will be very low.

Aqueous ammonia concentrations of 200 to 1300 mg/ℓ are possible in FGD sludge liquors when SCR ammonia emissions are 30 ppm, depending on the coal type. For this reason, leachate from FGD sludge ponds could cause contamination of groundwaters due to the ammonia. However, the amount of ammonia that would reach groundwaters from FGD and ash disposal ponds is unknown. Again, with proper pond lining these concerns would be eliminated. Depending on the pond pH and aqueous ammonia concentration, gaseous ammonia evolution could also occur from the sludge ponds. In some cases, biological treatment or stripping of pond discharge water may be necessary.

Gaseous ammonia or ammonia salts could theoretically result in visible plume formation; however, the majority of the ammonia salts will be removed in a cold-side ESP or baghouse, minimizing the chance of a plume. Systems using a hot-side ESP may have ammonium sulfate/bisulfate plume formation problems. A high pressure drop mist eliminator may be capable of preventing visible plume formation by removing the fine ammonia particulates passing through the FGD system, but would increase the FGD system capital costs about 5 percent (based on limestone). Another potential source of visible plume formation is the reaction of gaseous ammonia with $SO_2(g)$ leaving the stack gas. This phenomena is not expected to occur except at high levels of excess ammonia (>10 ppm) exiting the FGD system. These levels of ammonia emissions can exist with Western coal fired systems when the steady state SCR ammonia emissions are >50 ppm. This level of SCR emissions is higher than the guaranteed levels and would only be expected during upset conditions which is a transient, short-term situation. With Eastern coal, stack gas ammonia concentrations are expected to always be <<10 ppm. Japanese installations utilizing either SCR or ammonia injection for ash conditioning have indicated that plume formation is not a problem.

1.4 HEALTH EFFECTS

The health and environmental effects of a SCR will be minimal if standard operating and safety procedures are followed. Low levels of ammonia are neither toxic nor carcinogenic; however, an objectionable odor can occur at even low concentrations. The OSHA Permissable Exposure Limit for ammonia is 50 ppm. Although this level could occur during upset conditions, ammonia concentrations should be significantly lower during normal, continuous operation. A major spill of ammonia, however, could result in a locally toxic atmosphere for plant personnel.

1.5 CONCLUSIONS

1.5.1 Ultimate Fate of Ammonia

- Much of the ammonia will react with SO_3 and HCl to form salts which will be significantly reduced by downstream particulate removal equipment. 90-95 percent of the NH_3 should react to form these salts for exit SCR levels of 10-20 ppm NH_3, and 10-20 ppm SO_3.

- The removal of gaseous ammonia by FGD systems will depend heavily on the scrubbing liquor pH. Removal efficiencies for limestone systems were calculated to be about 50 percent for Western coal and about 94 percent for Eastern coal (assuming FGD inlet gaseous ammonia levels of 10-20 ppm). At the normally expected FGD inlet NH_3 concentrations of 1-3 ppm, higher removals would be realized. Other FGD systems which operate at higher pH levels than limestone systems should experience lower gaseous ammonia removal efficiencies.

- The removal of ammonium sulfate and bisulfate particulates in an FGD system will depend on the contactor type. Open contactors such as spray towers (used in many limestone systems) should not achieve high ammonia particulate removals since they are typically submicron particles. Higher pressure drop contactors such as packed or mobile beds could potentially achieve higher removals.

1.5.2 Equipment and Operational Impacts

- The ammonia salts formed will most likely improve ESP performance.
- Under high transient ammonia concentrations, gaseous ammonia would pass through the ESP. Some older plants have reported difficulty in cleaning the collection plates under these conditions.
- The removal of the submicron ammonia salts by a baghouse should be as efficient as for other small particulates (>99 percent). However, the presence of liquid ammonium bisulfate could cause blinding of the filter media and result in increased bag cleaning and replacement for baghouses immediately following the air preheater.
- Ammonia absorbed by the FGD will be beneficial with respect to SO_2 removal. At the expected NH_3 concentration of 1-3 ppm into the FGD unit, the SO_2 removal may be slightly increased. For higher ammonia concentrations, the increased absorbing capacity of the liquid could allow a reduction in L/G while maintaining constant SO_2 removal.
- Regenerable FGD systems may require special equipment to separate the by-product from ammonia compounds.

1.5.3 Waste Stream Impacts

- Under normal operating conditions ammonia emissions at the stack will be negligible. These low ammonia emissions should eliminate the potential for plume formation at the stack.
- Wet handling of the collected fly ash could generate aqueous and gaseous ammonia emissions, depending on the slurry pH and process configuration.
- Under normally expected FGD inlet concentration of NH_3 (1-3 ppm) and upstream collection of particulates after the air preheater, no significant environmental emissions are expected. Continuous high levels of ammonia (>50 ppm) in the SCR exit gas could result in high ammonia concentrations in the sludge pond water.

- Pond discharges could result in significant aqueous ammonia emissions. To avoid these emissions, the ash sluice system could be operated in a closed-loop mode with all ash pond overflow recycled to sluice ash. Another alternative is to reuse a portion of or all of the ash pond overflow elsewhere in the plant, such as for FGD system makeup. Stripping and/or biological treatment may be required for ammonia removal from wastewater. Secondary gaseous emissions from the pond could also occur, depending on the liquid pH and process configuration.

SECTION 2

INTRODUCTION

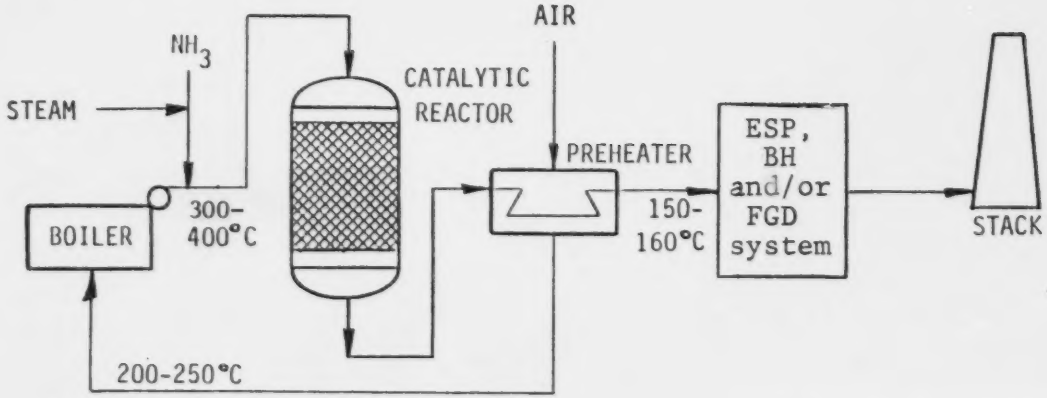
Recent Japanese experience with selective catalytic reduction (SCR) for controlling nitrogen oxides (NO_x) emissions from gas- and oil-fired combustion sources has shown that NO_x reductions of 80 to 90 percent are achievable.[1,2] Since this NO_x reduction exceeds that of combustion modifications alone, the Environmental Protection Agency (EPA) is interested in demonstrating SCR technology in the United States. The EPA has funded two pilot-scale demonstration projects for evaluating SCR process applicability to coal-fired combustion sources.

For a utility application of SCR (see Figure 2-1 for typical flue gas treatment configuration), the catalytic reactor is located between the economizer and air preheater sections of the boiler. At this point the flue gas temperature ranges from 300 to 400°C (570-750°F) which is suitable for the NO_x reduction reactions to occur rapidly. Ammonia is injected into the flue gas upstream of the catalyst and reacts with NO_x on the catalyst surface to form elemental nitrogen and water. Steam is used as the carrier for the ammonia to aid in dispersion after injection. The overall reactions can be represented by Equations 2-1 and 2-2.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (2\text{-}1)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad (2\text{-}2)$$

Typically, for 90% NO_x removal, the NH_3:NO_x mole ratio is 1:1.



ESP - Electrostatic precipitator
BH - Baghouse
FGD - Flue gas desulfurization

Figure 2-1. Typical arrangement - NO_x SCR Unit with boiler and other flue gas cleaning processes.

Although SCR systems have undergone extensive commercial development in Japan, an unresolved issue is that of ammonia emissions from the process and the impact of these emissions on equipment located downstream of the catalytic reactor. Such equipment can include air preheaters, flue gas desulfurization systems and particulate removal devices. EPA has conducted two studies of the effects of excess ammonia on downstream equipment. This report presents the results of the study examining these effects on baghouses, electrostatic precipitators, and flue gas desulfurization systems. A separate investigation was conducted to examine the impact of excess ammonia on air preheaters.[3]

2.1 PROBLEM DEFINITION AND PROJECT OBJECTIVES

Unreacted ammonia will exit the SCR system in concentrations normally expected to be about 10-20 ppm. However, under transient operating conditions, ammonia levels may be higher. Ammonium sulfate salts can form in downstream equipment due to the reaction of ammonia, sulfur trioxide, and water present in the flue gas as illustrated by Equations 2-3 and 2-4.

$$NH_3(g) + H_2O(g) + SO_3(g) \rightleftarrows NH_4HSO_4(\ell,s) \qquad (2\text{-}3)$$

$$2NH_3(g) + H_2O(g) + SO_3(g) \rightleftarrows (NH_4)_2SO_4(s) \qquad (2\text{-}4)$$

$$NH_3(g) + HCl(g) \rightleftarrows NH_4Cl \quad (s) \qquad (2\text{-}5)$$

The direction in which these reactions proceed is dependent on the flue gas temperature and the concentrations of the reactants. At a given flue gas concentration, the formation of the solid sulfate and liquid bisulfate will occur as the flue gas is cooled. For typical concentrations of NH_3 and SO_3 downstream of an SCR unit, the approximate formation temperatures of $(NH_4)_2SO_4$ and NH_4HSO_4 range from 195°C to 210°C and 165° to 180°C, respectively. Typical air preheater operating temperatures for the flue gas range from over 300°C at the inlet to about 150°C at the air preheater outlet. Obviously, the thermodynamics of the formation reactions indicate that some $(NH_4)_2SO_4$ and NH_4HSO_4 can form in the air preheater. Some of these ammonium salts will deposit on the preheater heat exchange surface but most will pass through and enter the downstream particulate control equip-

ment. Most of the particulates will be removed here but unreacted ammonia and traces of the ammonia salts will continue into the FGD system.

The formation and deposition of ammonium sulfates in air preheaters has been observed downstream of SCR systems.[3] Deposits have also formed during tests of fly ash conditioning with ammonia for improved ESP performance.

This study was performed to investigate the impact of the ammonia leaving the NO_x SCR process on downstream flue gas cleaning processes. Operational effects on electrostatic precipitators (ESP), baghouses, and flue gas desulfurization (FGD) systems were investigated. In addition, the ultimate fate of the ammonia was investigated and a literature search performed on the health and environmental effects of ammonia and ammonium salts.

2.2 APPROACH

The analyses presented in this report are based on the application of a SCR system to coal-fired utility boilers. Both low sulfur Western and high sulfur Eastern coals are considered. Table 2-1 presents the typical coal analyses and flue gas flows and compositions used in this study. These data are representative of the flue gas entering the SCR with the flue gas treatment processing configuration specified in Figure 2-1. Table 2-2 presents the makeup water analysis used for the FGD system investigations.

The first step in this study was to conduct a literature search to obtain information concerning the problems and benefits which could result from the presence of ammonia in gases entering ESP and FGD systems, and to gather data concerning health effects of ammonia and ammonia salts. Information was also collected concerning the formation of ammonia salts via the reaction of ammonia with gaseous acidic species in the flue gas. Baghouse and ESP data were sought to determine the ability of these control devices to remove ammonia particulates.

TABLE 2-1. COAL ANALYSES AND FLUE GAS PARAMETERS FOR REPRESENTATIVE EASTERN AND WESTERN COALS

	Eastern		Western	
Coal compositions (wt %)				
Carbon		57.5		47.85
Hydrogen		3.7		3.40
Nitrogen		0.9		0.62
Chlorine		0.1		0.03
Sulfur		4.0		0.48
Ash		16.0		6.40
Oxygen		5.8		10.83
Moisture		12.0		30.40
HHV cal/g (Btu/lb)	5,606	(10,100)	4,451	(8,020)
Flue gas parameters [1]				
SO_2 (mole %)		.2929		.0398
SO_3		.0030		.0004
H_2O		8.190		11.92
CO_2		11.95		11.88
N_2		73.73		70.50
O_2		5.824		5.656
HCℓ		.00704		.00252
NH_3	.0100 - .0000		.0100 - .0000	
Fly ash, g/m^3 (gr/ft^3)	6.32	(2.77)	3.02	(1.32)
Flow,[2] NM^3/sec (scfm)	553	(1.17×10^6)	607	(1.29×10^6)

[1] At exit from SCR system
[2] Based on 500 MW net generating plant (550 MW gross generation)

Source: Ref. 4

TABLE 2-2. REPRESENTATIVE FGD SYSTEM MAKEUP WATER ANALYSIS

pH	7.3
Component (mg/ℓ as ion)	
Carbonate	84.4
Sulfate	60.0
Calcium	35.0
Magnesium	8.2
Sodium	12.0
Chloride	15.0
Nitrate	0.8

Source: Ref. 4

Since ammonia has been used for improving ESP performance, the literature available was used to determine the ultimate fate of the ammonia in ESP systems. This information was also used to identify potential operating problems and alternatives for avoiding the problems which may result from ammonia upstream of the ESP. Unlike ESP's, little information is available on the effect of ammonia compounds on baghouses. Ammonia particulate removals were therefore assumed to be the same as the ability of baghouses to remove fine particulates.

The investigation of the effect of ammonia on FGD system operation was performed by using the Radian Inorganic Process Simulation (RIPS) computer model. This model consists of a group of subroutines which can be used to simulate the unit processes and chemical phenomena in lime/limestone FGD systems. The computer model considers the following dissolved species:

1) calcium
2) magnesium
3) sodium
4) ammonia
5) phosphate
6) chloride
7) carbonate
8) nitrate
9) sulfite
10) sulfate

and calculates the equilibrium partial pressure of CO_2, SO_2, and NH_3 gases for a given aqueous solution composition. A more detailed discussion of the computer model is presented in the Appendix.

The computer model was used to determine ammonia removal efficiencies in limestone scrubbing systems applied to utility boilers firing the Eastern and Western coals characterized in Table 2-1. Simulations were performed for various concentrations of ammonia entering the FGD system (0 - 100 ppm) and were used to determine:

1) expected ammonia removal efficiency,

2) required liquid-to-gas ratio (L/G) to achieve 90 percent SO_2 removal,

3) required reaction tank volume to prevent scale formation, and

4) sludge compositions.

Expected variations which might result for other FGD processes were also addressed. However, a more detailed analysis of the limestone FGD process was performed due to the large number of commercial limestone systems currently in operation in the U.S.

SECTION 3

EFFECTS OF NO_x SCR SYSTEMS ON DOWNSTREAM PARTICULATE CONTROL EQUIPMENT

This section discusses the possible operational effects on electrostatic precipitators (ESP's) and baghouses caused by residual ammonia from an NO_x selective catalytic reduction (SCR) process. First, the effect of ammonia on ESP performance is addressed. The discussions in this section are based upon results of a literature survey which evaluated ESP operation with gases containing low ammonia concentrations. Then, the effect of ammonia on baghouse operation is considered. Unlike ESP's, where ammonia has been used to enhance particulate removals, little information is available on the effect of ammonia on baghouses. Therefore, the amount of ammonia and ammonium salts removed in baghouses was estimated based upon literature data for the removal of fine particulates.

3.1 ELECTROSTATIC PRECIPITATORS

One method which is used throughout the utility industry to improve ESP collection efficiency involves injecting a conditioning agent. Sulfur trioxide is often used because it lowers the resistivity of the fly ash. Ammonia has also been used successfully; however, measurements indicate that ammonia does not lower the resistivity. Instead, the formation of charged ammonium bisulfate particles increases the space charge around the electrodes resulting in improved collection efficiency.

3.1.1 Ultimate Fate of Ammonia Species

Ammonia exiting an SCR reactor can react with SO_3 to form ammonia salts. At lower temperatures, NH_3 can react with $HC\ell$. Thus, ammonia entering an ESP

can be present as an acid salt or gaseous NH . Table 3-1 presents some data for several ESP systems where ammonia is injected to enhance particulate removal efficiency. These data show that less than 10 percent of the ammonia fed is detected in exit flue gases as ammonia vapor and almost all is recovered as ammonium salts in the fly ash when the ammonia added is less than twice the SO_3 present. The data also show reduction of SO_3 content of the flue gases when ammonia is added. Obviously, rapid reaction of ammonia to form ammonium bisulfate or ammonium sulfate occurs. Kinetic calculations and laboratory studies confirm the fact that these compounds are the primary reaction products. Some literature data indicates that ammonia decomposition and hydrazine formation is also possible in the ESP corona discharge. Table 3-2 shows melting point, boiling point, and solubility data for these compounds.

TABLE 3-2. PHYSICAL/CHEMICAL DATA FOR AMMONIA SALTS

		Melting point* °C	Boiling point* °C	Water solubility (°C) g/100 cc	
Ammonium chloride	NH_4Cl	350d	520s	$29.4^{(0)}$	$77.3^{(100)}$
Ammonium sulfate	$(NH_4)SO_4$	513d	-	$70.6^{(0)}$	$103.3^{(100)}$
Ammonium bisulfate	NH_4HSO_4	146.9	490	100	-
Ammonium sulfite	$(NH_4)_2SO_4 \cdot H_2O$	d	-	$100^{(12)}$	-
Ammonium bisulfite	NH_4HSO_3	d	-	5	5
Hydrazine	N_2H_4	1.4	113.5	∞	∞

*d indicates decomposition as opposed to a phase change, s indicates sublimation.

Source: Ref. 6

At normal SCR and ESP operating temperatures, many of these compounds are unstable. Since decomposition of ammonium sulfites to produce NH_3 and SO_2 occurs at ESP temperatures, formation of these compounds is not likely.

TABLE 3-1. AMMONIA CONDITIONING FOR ESP IMPROVEMENT

Plant	Coal		Gas temp, °C	Injected NH_3, ppm	Flue gas[a] conc, ppm		Fly ash properties[a]			Small[a] particle conc,[c] no./cm³	ESP	
	% Sulfur	% Ash			SO_3	NH_3	SO_3, wt %	NH_3, wt %	pH[b]		Efficiency %	Outlet g/m³
Widows Creek	0.9	17.6	132	0	5	0.6[d]	0.22	<0.01	5.2	-	90	
				10	1	0.8	0.18	0.04	5.4	-	98	
Bull Run	1.2	17.0	127	0	2	<0.3	0.31	<0.01	4.5	2.4×10^6	-	
				7	1	<0.3	0.33	0.05	4.5	9.8×10^6	-	
Widows Creek	3.5	13.8	132	0	11	<0.1	1.24	<0.01	10.0	1.2×10^7	87	
				20	3	<0.1	1.31	0.12	10.0	3.1×10^7	>99	
Gallatin	4.0	14.2	132	0	9	<0.1	1.00	<0.01	8.6	2.2×10^7	-	0.35
				20	1	1.0	1.40	0.21	8.6	6.1×10^7	-	0.07

[a] All data for flue gases and fly ash were obtained with samples collected between the plane of ammonia injection and the inlet to the precipitator.

[b] Equilibrium value of an aqueous slurry of fly ash containing 1 part of ash to 300 parts of distilled water.

[c] Size range, 0.005 to 1.0 cm

[d] The magnitude of this value is anomalous. It probably reflects leakage of ammonia from the injection system after the main valve has been closed.

Source: Ref. 5

Ammonium sulfate decomposes with 1/3 of the ammonia evolved as NO_2 and/or N_2 at temperatures near 400°C, but is more stable as a solid at lower temperatures.[7] These data indicate that some ammonia salts such as ammonium sulfate and bisulfate will form as the temperature approaches the air preheater exit temperature.

Electrostatic precipitator operation involves the use of continuous corona discharges from a wire to a collecting plate causing ionization of gas molecules in the flue gas stream. These are primarily negative corona discharges although under poor operating conditions, back corona (positive) discharges occasionally occur. Frequent sparks (30/min to 100/min) are also expected at best operating conditions although sustained arcing is immediately suppressed, or prevented.[8] Voltages range from 30 kV to 100 kV and current flow is about 0.5 to 4 x 10^{-8} amp/cm (12 to 17 x 10^{-6} amp/ft^2) across the 7.5 cm (3 in) to 15 cm (6 in) space between discharge and collecting electrodes.[9] Exposure times are 15 to 54 seconds for typical ESP operation.[10]

The reactions of pure ammonia gas in electrical discharges have been studied in laboratory apparatus. Both decomposition of NH_3 to N_2 and H_2 and hydrazine (N_2H_4) formation have been observed. The decomposition reaction rate was 0.5 percent/min for 5 Kv and was 1 percent/min for 10 Kv at 25°C (77°F) at 50 mm Hg absolute pressure using alternating voltage in a wire and cylinder (1 cm spacing) reactor.[11] The specific decomposition rate increased linearly with the ratio, V/Vi, of the applied voltage (V), to the voltage at which discharge initiated (Vi). This relationship was independent of initial ammonia pressure over the range of 50 mm Hg absolute to 200 mm Hg absolute. No temperature change was observed during the experiments and only pressure, voltage and current relationships were studied. These data indicate that some decomposition of ammonia is to be expected at ESP operating conditions. Other studies in a flow reactor showed no hydrazine formation with negative corona, but up to 0.3 percent/min reaction to N_2H_4 with positive corona.[12,13] Negative corona is used in ESP's for industrial gas cleaning but under high resistivity dust conditions, a positive corona can develop temporarily. Very poor ESP collection efficiency results when back corona develops and corrective action is taken to eliminate it. While no significant formation of hydrazine is expected, analytical studies of ESP ash when ammonia is present

should include hydrazine content. As hydrazine is an excellent reducing agent, it is likely to be largely decomposed to N_2, H_2, and ammonium ions by the other constituents of the ash.[14]

For NH_3 levels exiting the SCR of 10-20 ppm, gases leaving the ESP can be expected to contain less than 0.01 g/m^3(0.0043 gr/ft^3) of ammonia containing species, assuming 90 percent of the inlet ammonia forms ammonium salt particulate and 95 percent of this is recovered in the ESP.[5] Data from studies of ammonia injection indicate that one half of the ammonia forms particulate matter less than 0.05 microns in diameter and most of this material is collected as fly ash in ESP hoppers.[15] Data from one such test shows that about 2 percent of the equivalent ammonia salt particulate matter leaves the ESP as fine particles (<0.38 micron) when 20 ppm ammonia is injected.[15] The ammonia species in uncollected particulates is not expected to exceed 10 percent of the particulate mass. Compounds such as ammonium sulfate and ammonium bisulfate are expected to be essentially all of the emitted ammonia solids.

In summary, the ultimate fate of ammonia entering an ESP from an SCR system is that 5 to 10 percent of it will leave in ESP exit gases as ammonia salts and gaseous ammonia, and 90 to 95 percent will be collected as ammonia salts with the fly ash.

3.1.2 Operational Effects (Eastern and Western Coals)

The primary effect of SCR systems is to reduce the NO_x content of the flue gases. Presence of NO_x in flue gases entering an ESP has no known effect on ESP operation. It is anticipated that the 90 percent reduction in NO_x content of the flue gas will have a negligible direct effect on ESP performance and on characteristics of the fly ash collected.

The secondary effects of SCR systems are to add ammonia to the gas stream and to increase its SO_3 content. This increase is due to SO_2 oxidation

by the NO_x catalyst. Both ammonia and SO_3 (and their salts) have been used as conditioning agents to improve ESP operation in cases of poor performance due to high ash resistivity. For low sulfur coals, addition of ammonia, sulfamic acid, ammonium sulfate, ammonium bisulfate and sulfuric acid as aqueous solutions and dry sulfur trioxide have all been used as conditioning agents in commercial applications. Ammonia conditioning, both as dry gas and as water solutions, has been used for some commercial installations burning high sulfur coals. Under design and normally expected SCR reactor operating conditions (less than 20 ppm ammonia exiting), only beneficial effects on ESP operation are expected. However, some detrimental effects on ESP operation have been occasionally noted when excessive ammonia additions are made. A review of commercial and pilot plant data was made to assess the possible problems which may be encountered.

Ammonia conditioning to improve ESP operation has been extensively tested and is in commercial use.[5,9,15,16,17,18,19] In all cases either no operational effect was noted or significantly reduced emissions were observed. In the U.S., ammonia levels up to 30 ppm have been used with most effective results being obtained at 10 to 15 ppm. Table **3-1** showed representative data for ammonia conditioning. Increased adhesion of particles has been observed with high sulfur coals causing less reentrainment.[15] British testing included 20 ppm additions with no detrimental effects. In Australia, concentrations of 40 to 60 ppm decreased emissions, but one older plant required periodic washing of collector plates to remove sticky fly ash.[19]

Ammonia salts have been shown to form rapidly from NH_3 with HCl and SO_3 present in the flue gases.[15] These salts are ammonium chloride, ammonium bisulfate and ammonium sulfate. Studies of direct addition of these compounds to flue gases show them to have resulted in improved ESP performance.[15,20,21,22] No ESP operating problems have been reported at additive rates equivalent to 25 ppm of ammonia for both high and low sulfur coal applications. Either the ammonia itself or the large numbers of fine particles (<0.5 μm) affects the electrostatic field as a "space charge" effect.[5] This may be the mechanism of improved operation with ammonia addition. The increased cohesiveness of the fly ash reduces the reentrainment of collected ash and contributes to improved ESP performance.[15] Since ammonium bisulfate has

a melting point below the normal ESP operating temperature of 150°C, the presence of this compound as a liquid film on the particulate may cause adhesion to other particles and to the collecting plates.

Ammonia injection resulted in excessive sparking in one case. Electrode misalignment was considered to be the dominant cause of this effect. It might be anticipated that in a similar situation excess ammonia from a NO_x SCR would have a detrimental effect until corrective action could be taken.[15]

Sulfur trioxide addition to flue gases is a common means of improving ESP operation when low sulfur coal is burned. Addition of SO_3 or H_2SO_4 up to 55 ppm has been shown to be beneficial.[15,16,17,19,22,23,24,25,26] The sulfur trioxide reacts with water in flue gases to form sulfuric acid and potentially can cause corrosion if the acid dewpoint is reached in the ESP. Figure 3-1 shows the acid dewpoint of sulfuric acid as a function of the moisture content and H_2SO_4 concentration.

The potential operating problems with ESP's downstream of SCR systems are summarized below:

1) Ammonia salts on fly ash may cause excessive adhesion to collection plates.

2) Increased SO_3 in the flue gas may cause corrosion of materials in the ESP due to sulfuric acid formation.

3) The presence of ammonia and/or ammonia salts may cause excessive sparking in cases with poorly aligned electrodes.

However, under normal operating conditions of 10 to 20 ppm of ammonia leakage from the SCR reactor and normal sulfur trioxide levels only improved operation of the ESP is anticipated.

Table 3-3 shows the calculated potential ammonia salt concentration in fly ash from the range of SCR ammonia leakages investigated. These values are similar to those demonstrated as operable in Table 3-1 at up to 50 ppm NH_3 leakage for Eastern coal and up to 20 ppm NH_3 leakage for Western coal.

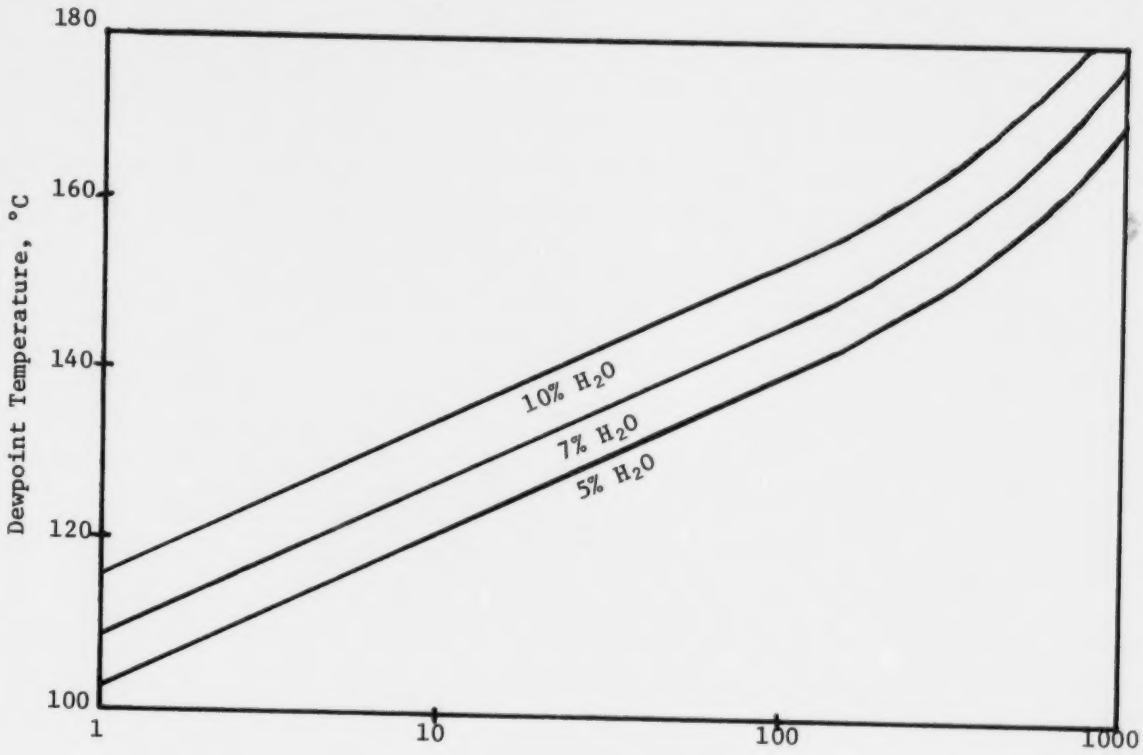


Figure 3-1. Sulfuric acid dewpoint as a function of flue gas H_2SO_4 concentration and moisture content.

Source: Ref. 6

TABLE 3-3. CALCULATED AMMONIA LEVELS IN COLLECTED FLY ASH*

NH_3 exiting SCR system, ppm	Wt % NH_3 on fly ash	
	Eastern coal	Western coal
10	0.05	0.10
20	0.09	0.20
50	0.23	0.50
100	0.46	1.00

*based on 90 percent of the NH_3 being removed in the ESP and adhering to the fly ash.

From Figure 3-1 the only case of potential acid corrosion would come at high H_2SO_4 concentrations coupled with extremely low (<130°C) ESP operating temperatures.

3.2 BAGHOUSES

Baghouses used for particulate control will be located downstream of the SCR reactor and air preheater. They will be placed either upstream of a wet FGD system or downstream of a spray dryer FGD process. The following discussion applies to either location.

3.2.1 Ultimate Fate of Ammonia Species

Specific ammonia removal data are not available for baghouses as was the case for ESP's where ammonia injection has been used to enhance particulate removal. Very fine ammonia salts (formed from reactions of NH_3 with HCℓ and SO_3) are expected at the baghouse operating temperature (150-65°C). However, baghouses are capable of controlling submicron particles with approximately 99 percent efficiency. The collection mechanism for larger particles (>1 μm) is impaction and electrostatic attraction, while Brownian diffusion becomes the controlling factor for particles less than 0.2 μm.[27,28]

Brownian diffusion is proportional to gas velocity and will, theoretically, be dependent on the air-to-cloth ratio.[28,29] The air-to-cloth ratio is the volumetric flowrate of flue gas divided by the surface area of the filter fabric. The impact of this ratio on the collection efficiency of particles ranging in size from 0.1 to 10 μm is illustrated in Figure 3-2. The dotted lines in the figure represent expected increases in removal efficiency as particle size decreases. This increase is shown in Table 3-4 for particles smaller than 0.36 microns.

The particulate collection efficiencies of a commercial-scale baghouse are presented graphically in Figure 3-3. The median overall collection efficiency was consistently above 99.4 percent.

TABLE 3-4. DUST REMOVAL EFFICIENCIES OBTAINED DURING PILOT PLANT TESTS

Nomex Felt Filter Media With Air-to-Cloth Ratio of ∿6	
Particle Diameter, μm	Removal %
>9.5	99.84
6	99.74
4	99.78
2.8	99.69
1.75	98.03
0.9	99.21
0.54	99.16
0.36	96.88
<0.36	98.98

Source: 28

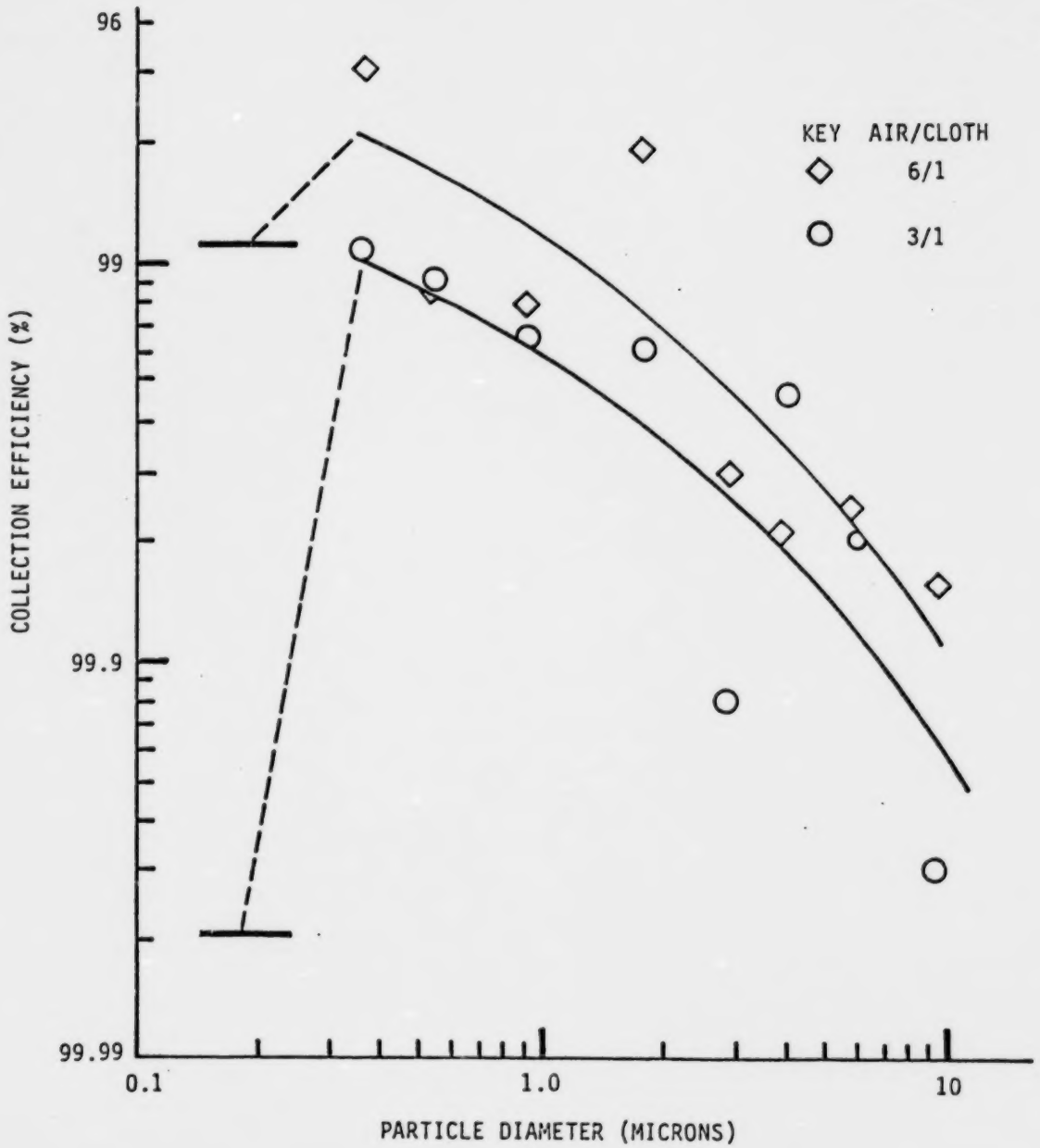


Figure 3-2. Fabric filtration collection efficiency vs. particle diameter.

Source: 28

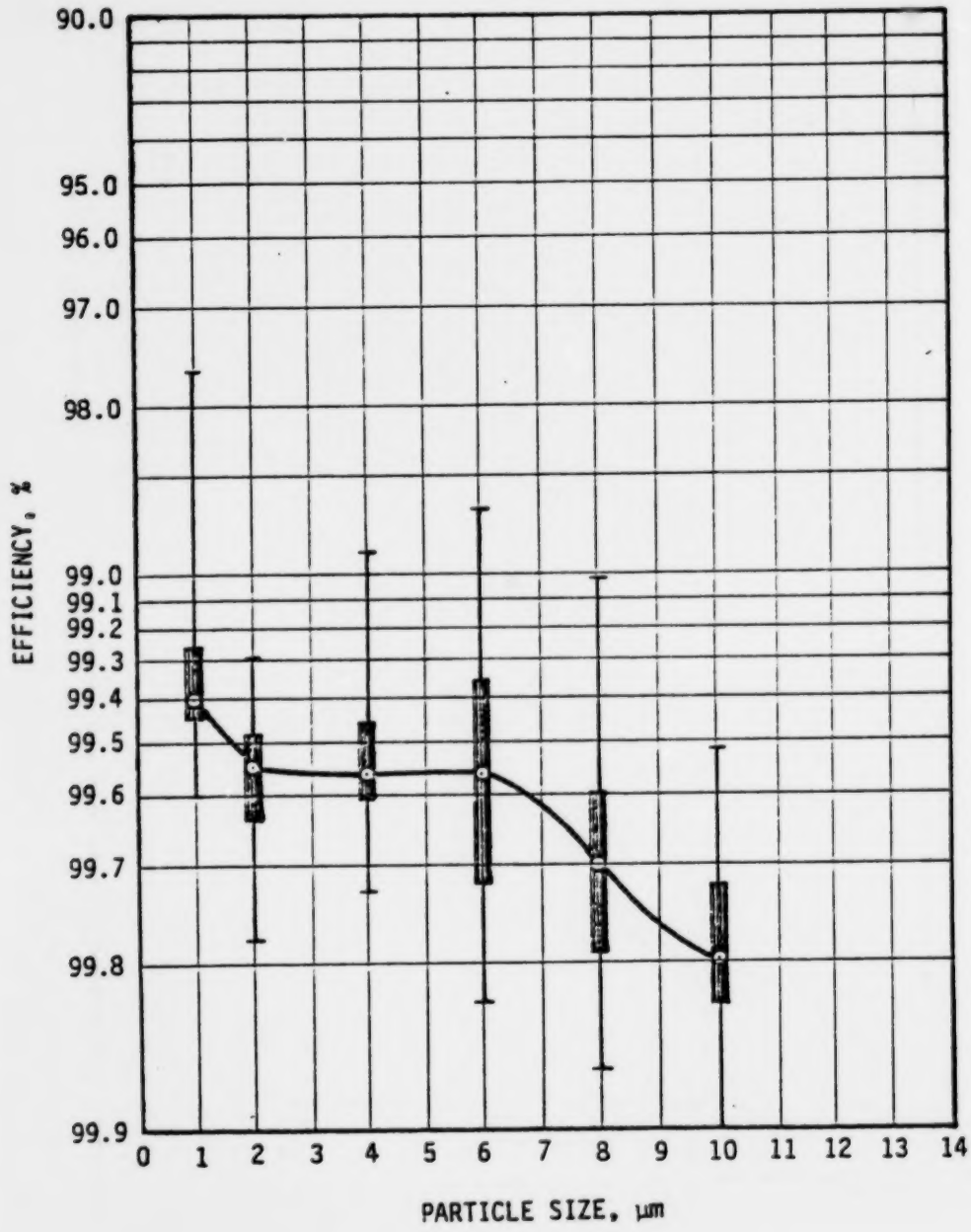


Figure 3-3. Median fractional removal efficiency for 22 baghouse tests.

Source: 30

In summary, little data is available on the removal of ammonia particulates in baghouses. Pilot plant tests are being conducted on a NO_x SCR system in Japan to study filter operation. Data are expected to be available in 1981.[1] Based upon the ability of baghouses to remove submicron particles, high ammonia particulate removals are expected. The baghouse may remove more of the NH_3 gas than the ESP does because this gas will contact previously collected particulate in the bag filter cake. It is anticipated that ammonia salts will be controlled in the same manner as other submicron particles. Consequently 99 percent or greater removal of ammonia sulfate/bisulfate is predicted for the baghouse.

3.2.2 Operational Effects (Eastern and Western Coals)

Ammonia salts may result in a stickier fly ash due to their hygroscopic nature. This could make filter cleaning more difficult. A higher pressure drop may also occur if the submicron particles penetrate the bag fabric and cause blinding. If significant blinding does occur, the cleaning frequencies will have to be increased to keep the pressure drop below acceptable levels. Ammonia particulates could potentially lead to more frequent bag replacements.

The severity of these potential problems is difficult to quantify based upon the limited information currently available. Ammonia in the flue gas should not increase the baghouse performance as it may with ESP's. Further investigation, such as pilot or full scale testing, will be required before the severity of the effect of residual ammonia on baghouse operations can be quantified.

SECTION 4

EFFECTS OF NO_x SCR SYSTEMS ON DOWNSTREAM FLUE GAS DESULFURIZATION EQUIPMENT

The effects of excess ammonia from NO_x SCR units on downstream Flue Gas Desulfurization (FGD) systems were determined by using the Radian Inorganic Process Simulation Computer Model (RIPS). This model consists of a group of subroutines which simulate the various major pieces of equipment and the chemical phenomena occurring in FGD systems.

Based upon a specified SO_2 removal efficiency, the RIPS model can be used to estimate process stream compositions and flows, the required liquid-to-gas (L/G) ratio to achieve the SO_2 removal, and the reaction tank volume required to prevent chemical scaling. L/G's are calculated such that sufficient liquid phase alkalinity is present to maintain an adequate driving force between the flue gas and scrubbing liquor for SO_2 removal. Mass transfer area or gas side film limitations are not considered. Reaction tank volumes are calculated to allow the system to meet the solids precipitation requirements ($CaSO_4 \cdot 2H_2O$, $CaSO_3/SO_4 \cdot \frac{1}{2}H_2O$) via a crystal growth mechanism where precipitation occurs on existing solids. Underdesigned systems which experience significant nucleation of the solid sulfur species (versus crystal growth) usually encounter scaling conditions in the scrubber.

Table 4-1 lists the key assumptions inherent in the RIPS model. A more detailed discussion of the model is presented in the Appendix. Table 4-2 describes the overall design basis for the simulation cases.

It should be emphasized that the results presented here do not represent optimum scrubber designs. Scrubbers in series (double loop operation) or the use of additives to lower L/G requirements were not considered. Rather,

simulations were performed purely for comparative purposes to examine the effect of various ammonia levels on the FGD system.

TABLE 4-1. KEY ASSUMPTIONS IN RIPS MODEL

1. The scrubber behaves as an adiabatic contacting device.
2. The partial pressures of CO_2 and H_2O in the gas leaving the scrubber are in equilibrium with the scrubber liquid at the scrubber temperature.
3. No precipitation occurs in the scrubber. However, dissolution of certain solid species such as $CaCO_3$ is allowed.
4. The temperature of the recirculating process liquor streams is fixed at the adiabatic saturation temperature of the scrubber effluent liquor.
5. The temperature of the water make-up has no effect upon the circulating liquor temperature.
6. Ionic reactions taking place in the liquid phase are rapid and thus are at equilibrium.
7. The holding time of the solid-liquid separator is sufficiently long that solid-liquid equilibrium is achieved.
8. The reaction tank closely approaches an idealized backmixed vessel.

At the time this study was initiated, accurate estimates of the percent conversion of $NH_3(g)$ to ammonia salts upstream of the FGD system were not available. Ammonia salts in the flue gas are typically submicron in size and are not effectively removed by most wet scrubbing processes. Therefore, they will have little impact on the operation of the FGD system. Since the purpose of this study was to identify any potential problems in the downstream flue gas cleaning equipment, all of the ammonia present was assumed to be present as $NH_3(g)$ (a "worst case" situation). Potential problems could then be readily identified and the severity of these problems better evaluated once data became available on the degree of conversion of $NH_3(g)$ to ammonia salts.

TABLE 4-2. COMPUTER SIMULATION DESIGN BASIS

	Eastern Coal	Western Coal
% SO_2 removal	90	90
% Sulfite Oxidation	25	90
% NH_3 removal	Varied based upon a gas-liquid concentration driving force for ammonia removal.	
Liquid-to-gas ratio (L/G)	Varied to obtain the specified SO_2 removal based upon maintaining a sufficient gas-liquid concentration driving force.	
Reaction tank volume	Sized to insure that the $CaSO_4 \cdot 2H_2O$ (gypsum) relative saturation does not exceed 1.3 in the scrubber effluent. Scaling conditions are usually associated with relative saturations greater than 1.3-1.4 for gypsum.	
Limestone Stoichiometry (moles Ca/mole SO_2 removed)	1.1	1.1
Wt % solids		
Scrubber loop	10	10
Waste sludge	50	50

Based upon subsequent data, obtained after the computer simulation work and first draft of this report were completed, it appears that most of the ammonia will be present as ammonia salts at typical FGD operating temperatures. Therefore in commercial installations, the majority of the ammonia (present as ammonia salts) will be removed by an ESP or baghouse. Typical ammonia loadings to the FGD system should be on the order of 1-2 ppm based upon excess ammonia levels from the SCR unit of 10-20 ppm.

A limestone scrubbing system (see Figure 4-1) was used as the comparison basis for the evaluation since the majority of the scrubbers currently in operation on U.S. utility boilers are lime or limestone processes.[31] In general, other scrubbing systems should experience similar effects although ammonia ($NH_3(g)$) removals may vary with the type of system due to variations in the scrubbing liquor pH and type of gas-liquid contactor. Other FGD systems such as lime, magnesium oxide, and sodium-based processes typically operate at higher pH's than limestone systems. Since ammonia removal decreases at higher liquor pH's, the removals and resulting liquid ammonia concentrations calculated for limestone systems should be higher than most other FGD systems. Spray dryers should not be adversely affected by unreacted ammonia. Any ammonia salts which form should be removed by the baghouse (used in conjunction with the spray dryer) as discussed in the previous section.

4.1 ULTIMATE FATE OF AMMONIA SPECIES

Ammonia exiting the SCR system can react with SO_3 in the flue gas to produce ammonia salts (i.e., $(NH_4)_2SO_4$, NH_4HSO_4). These salts form particulates which are typically submicron in size[32,33,34,35] and may exist either as a solid or liquid depending on the species and gas temperature. If the FGD system is downstream of an ESP, 90-95 percent of these particulates will be removed by the ESP. Baghouses should remove essentially all of the ammonia particulates. In limestone scrubbing systems, spray towers are typically used because they have few internals and do not require substantial gas-side pressure drop. As a result, ammonia particulates which reach a limestone FGD system will most likely pass through the scrubber without being removed. High pressure drop scrubbers are normally required to achieve any significant removal of submicron particles.[6] In FGD systems which use packed or mobile bed scrubbers, some removal of the ammonia salts may occur.

The RIPS simulation model was used to predict the level of gaseous ammonia which will be absorbed by the FGD system. In order to determine the maximum effect of ammonia on the FGD system, several assumptions were made. First, all of the ammonia entering the FGD system was assumed to be present

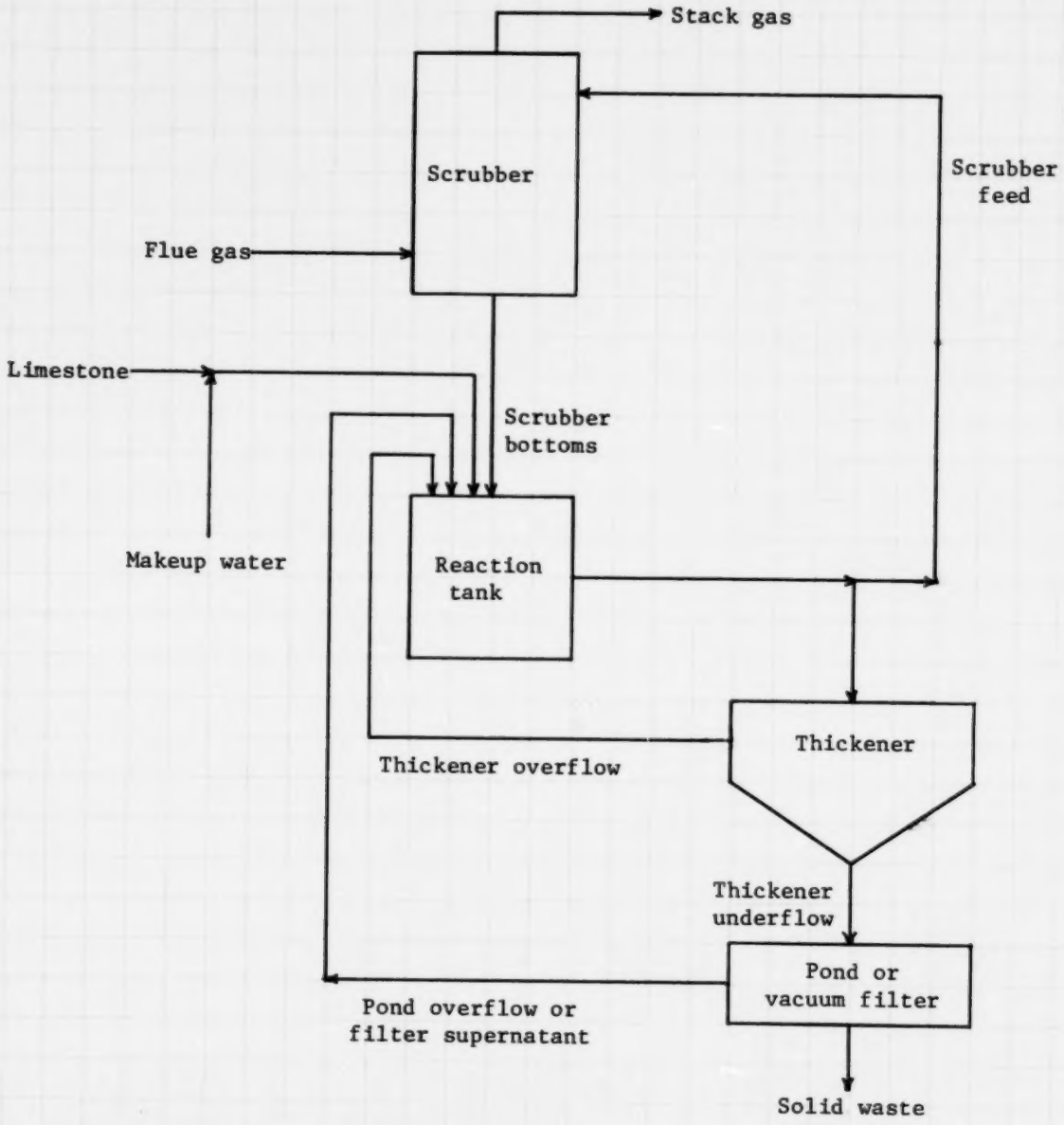


Figure 4-1. Simplified limestone wet scrubbing process.

in the gas phase in modeling the FGD system. Additionally, no ammonia removal was assumed to occur in upstream particulate control equipment. The maximum ammonia concentration in the scrubbing liquor will be predicted under these conditions since gaseous ammonia will be removed to a much greater degree than the ammonia particulates. Thus, modeling the system under these conditions represents a "worst case" situation with respect to the effect of ammonia on FGD system operation.

Ammonia concentrations entering the scrubber were varied from 0-100 ppm. The level of ammonia removal for each case was calculated assuming the system was not mass transfer area limited. Removals were based upon maintaining a sufficient concentration driving force between the gas and liquid phase. This describes a "worst case" approach and will predict the maximum ammonia levels in the scrubbing liquor.

Computer simulations were run at inlet $NH_3(g)$ concentrations of 0, 10, 20, 50, and 100 ppm for both Eastern and Western coal applications (see Tables 2-1 and 2-2 for coal and water analyses). In actual operation 1-2 ppm of gaseous ammonia would be expected in the gas entering the FGD system (for SCR NH_3 leakage of 10-20 ppm). However, under upset conditions, ammonia levels may approach 100 ppm. Since the RIPS model necessarily assumes steady state conditions, the transient nature of upset conditions could not be accurately modeled. But the assumption of steady state does serve to bound the impact of the higher transient ammonia levels (50 ppm, 100 ppm) since the maximum ammonia concentrations in the FGD system will be reached when the system is at steady state.

Tables 4-3 and 4-4 show the predicted ammonia removals and sludge liquor compositions for each of the ten cases considered. The solids concentration in the waste sludge was assumed to be 50 weight percent. Different solids concentrations will result in significantly different ammonia and other dissolved solids concentrations in the sludge liquor. A solids content of 25 percent in the sludge will reduce the ammonia concentration by approximately 70 percent while a solids content of 80 percent will increase the ammonia concentration about 300 percent, relative to the 50 weight percent sludge.

TABLE 4.3 PREDICTED AMMONIA REMOVAL AND SLUDGE LIQUOR COMPOSITION FOR TYPICAL WESTERN COAL[1]

Case	Inlet gas NH_3, ppm	% NH_3 removal	Sludge liquor composition, mg/ℓ as ion									
			Ca	Mg	Na	Cl	HCO_3	SO_3	SO_4	NH_3	pH	$P^*_{NH_3}$ (ppm)
1	100	25	2010	162	238	14,200	836	1277	3744	6580	6.2	96
2	50	35	3340	163	238	14,200	240	554	2240	4615	6.0	48
3	20	45	5565	164	240	14,290	238	286	1500	2390	5.9	18
4	10	55	6560	165	241	14,340	195	188	1340	1466	5.9	10
5	0	0	8220	165	242	14,400	187	93	1170	0	5.8	0

[1]Values based on Ca/SO_2 stoichiometry of 1.10 (mole basis), 90% sulfite oxidation, 90% SO_2 removal and 50% solids in waste sludge.

TABLE 4-4. PREDICTED AMMONIA REMOVAL AND SLUDGE LIQUOR COMPOSITION FOR TYPICAL EASTERN COAL.[1]

Case	Inlet gas NH_3, ppm	% NH_3 removal	Sludge liquor composition, mg/ℓ as ion									
			Ca	Mg	Na	Cl	HCO_3	SO_3	SO_4	NH_3	pH	$P^*_{NH_3}$ (ppm)
1	100	85	1180	35	50	6240	836	834	3380	3550	6.0	25
2	50	90	2124	35	50	6264	528	255	1711	1887	5.9	12
3	20	93	3158	35	50	6288	419	100	1251	783	5.9	4
4	10	95	3554	35	50	6297	368	66	1157	400	5.9	2
5	0	0	3984	35	50	6306	332	47	1078	0	5.9	0

[1]Values based on Ca/SO_2 stoichiometry of 1.10 (mole basis), 25% sulfite oxidation, 90% SO_2 removal and 50% solids in waste sludge.

For the typical Western coal, the $NH_3(g)$ removal efficiency varied from 25 percent in Case 1 (100 ppm inlet NH_3) to 55 percent in Case 4 (10 ppm inlet NH_3). Corresponding ammonia concentrations in the sludge liquor were 6580 mg/ℓ (Case 1) and 1466 mg/ℓ (Case 4). For the Eastern coal, the $NH_3(g)$ removal efficiency ranged from 85 percent for the 100 ppm inlet case to 95 percent for the 10 ppm inlet case. Ammonia concentrations in the sludge liquor were 3550 mg/ℓ (100 ppm case) and 400 mg/ℓ (10 ppm case) respectively. Also shown in Tables 4-3 and 4-4 is the calculated equilibrium partial pressure of ammonia ($P^*_{NH_3}$) above the sludge liquor. This value should not be confused with the $P^*_{NH_3}$ above the scrubbing liquor. The $P^*_{NH_3}$ above the scrubbing liquor will be much lower due to the lower pH in the scrubber. The sludge, however, is at solid/liquid equilibrium and consequently a higher pH. The $P^*_{NH_3}$ above the sludge gives an indication of the tendency of the ammonia to evolve into the atmosphere as $NH_3(g)$. Higher values of $P^*_{NH_3}$ indicate a stronger tendency for the ammonia to evolve. The significance of ammonia evolution and $P^*_{NH_3}$ as a function of pH are discussed in Section 5.

Figures 4-2 and 4-3 show the steady state ammonia concentrations in the sludge liquor graphically for the different inlet levels of NH_3 in the flue gas. Also shown on these figures, and others, are the anticipated operating range that will occur under the normal, steady state conditions of 10 to 30 ppm of ammonia in the gas leaving the SCR reactor. Most of this ammonia will form salts as the gas cools and be removed by the ESP or baghouse. For Western coal, this removal amounts to 70% and for Eastern coal it is 90%. Therefore, if 30 ppm of ammonia are emitted by the SCR system, the concentration at the scrubber inlet will be 9 ppm for Western coal and 3 ppm for Eastern coal. These ammonia concentrations were used to determine the expected operating ranges shown on the figures. For example, for the worst case of 30 ppm of ammonia leaving the SCR system the steady state concentration of ammonia in the FGD sludge liquor will be about 1300 mg/ℓ for Western coal (Figure 4-2) and about 200 for Eastern coal (Figure 4-3). Even though the percent removal of ammonia by the FGD system is lower for Western coal, higher ammonia concentrations are observed due to the lower solid waste disposal requirements. Lower disposal requirements were calculated for Western coal cases because less SO_2 is being absorbed by the system, therefore forming less sludge.

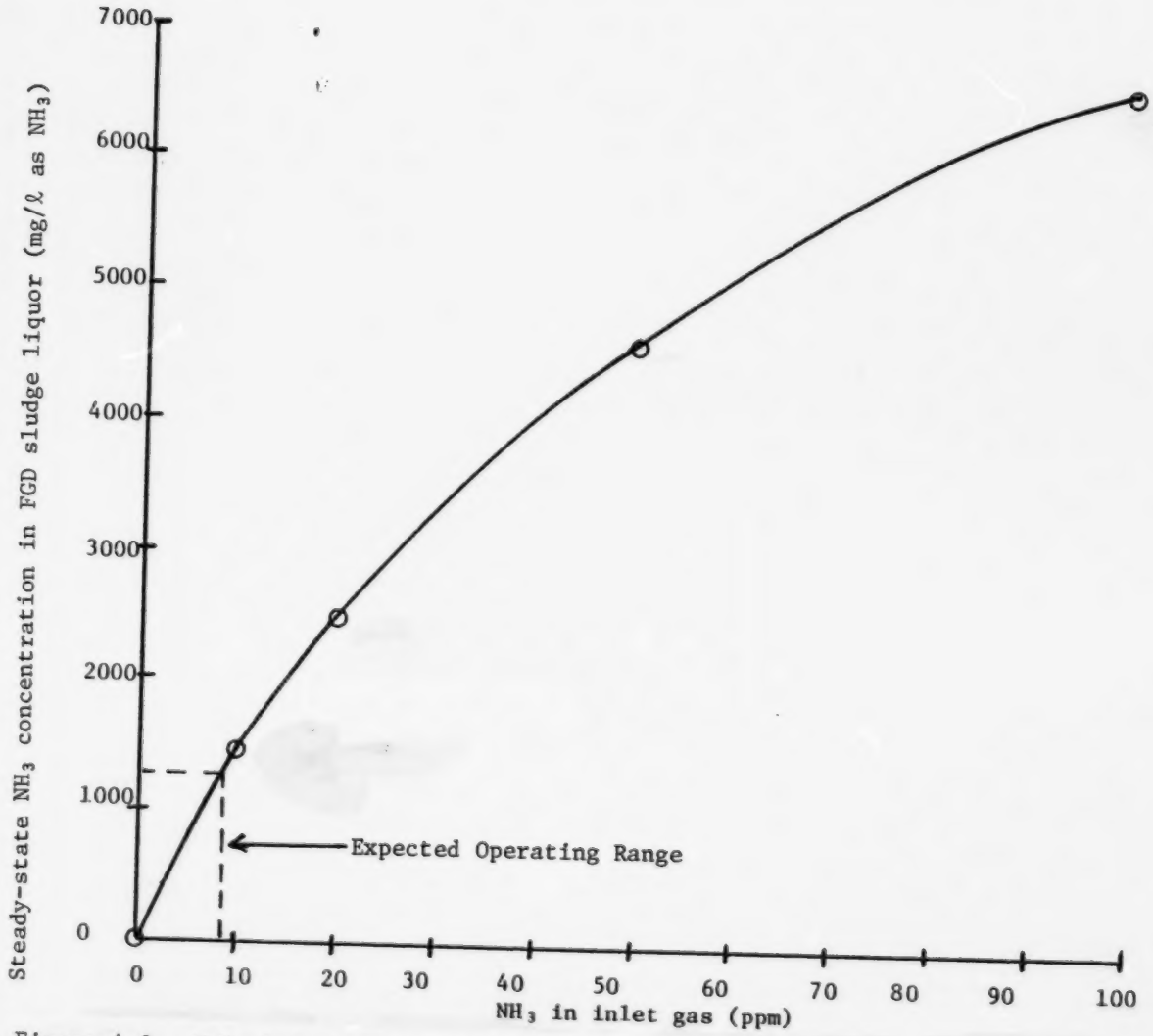


Figure 4-2. Calculated NH_3 concentration (steady-state) in limestone scrubber sludge vs NH_3(g) in inlet gas (Western coal).

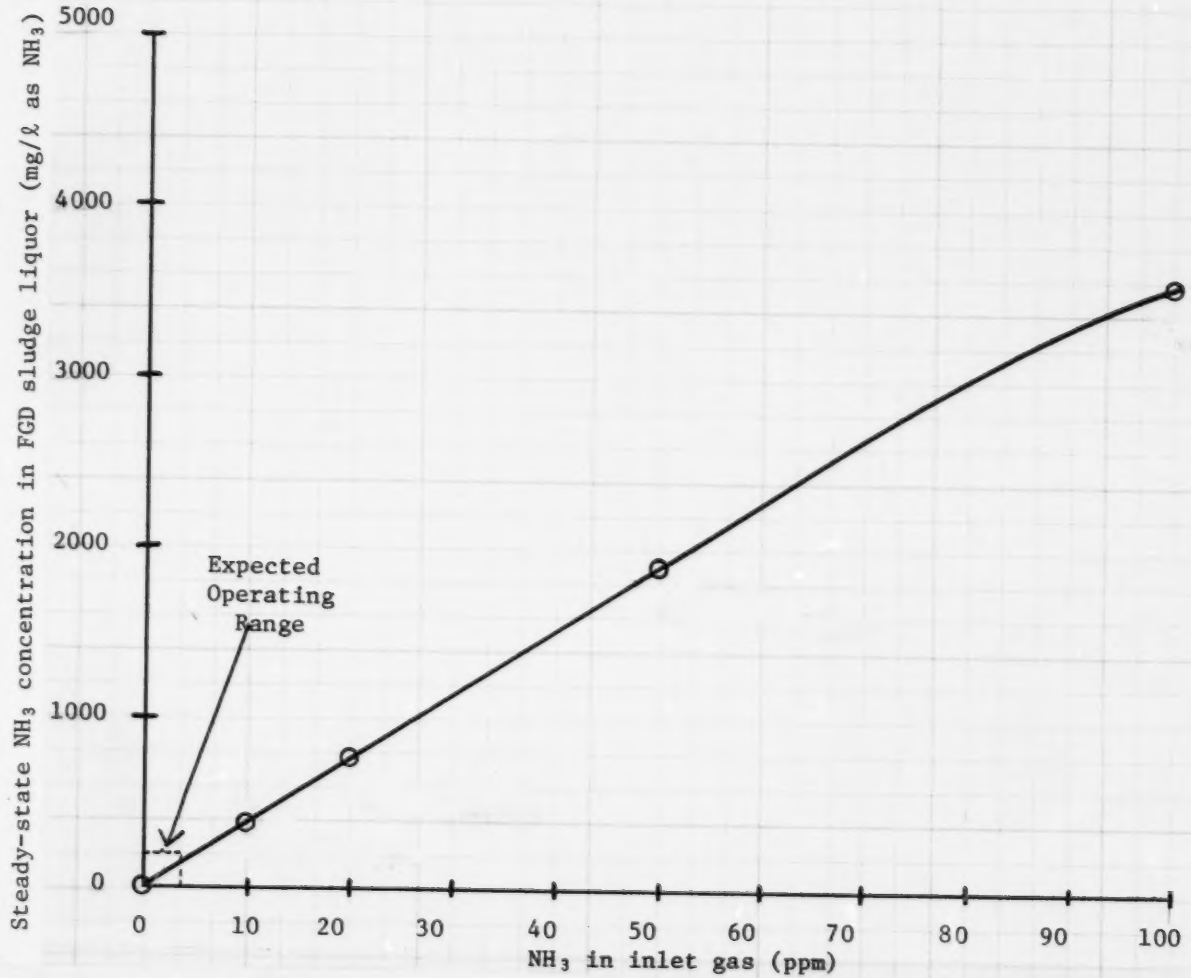


Figure 4-3. Calculated NH_3 concentration (steady-state) in limestone scrubber sludge vs NH_3(g) in inlet gas (Eastern coal).

Figures 4-4 and 4-5 graphically show the ammonia removal efficiencies predicted as a function of the inlet flue gas ammonia concentration. Lower NH_3 removals are predicted for the Western coal cases than for the Eastern coal cases due to the higher steady state ammonia concentrations in the scrubbing liquor which result in a lower driving force for removal. Also, lower liquid-to-gas ratios (L/G's) are required in the Western coal cases to achieve 90 percent SO_2 removal which causes lower ammonia removal efficiencies.

The levels of ammonia in the liquid phase calculated by the computer are steady state values. The computer model does not allow for transient inlet ammonia gas concentrations or other factors which could change the liquid phase ammonia levels. Under expected operating conditions with 1-3 ppm NH_3 in the flue gas, the ammonia concentration in the liquid phase would be much lower than those predicted for the 10 ppm cases. Additionally, as stated previously, the percent solids in the pond has a major effect on the steady state level of dissolved species in closed loop systems. If a groundwater hazard due to leaching from the sludge pond is present, it may be necessary to remove the ammonia. Depending on the concentration and flow rate, either ammonia stripping or biological treatment could be used to reduce the circulating ammonia levels. A detailed discussion of these treatment processes is beyond the scope of this study.

4.2 OPERATIONAL EFFECTS

The effects of ammonia in the flue gas entering the FGD system on SO_2 removal, scaling potential, and solids dissolution and precipitation are discussed for a limestone FGD system in this section. Ammonia levels in the inlet flue gas from 0-100 ppm were investigated for typical Eastern and Western coal applications. All the ammonia was assumed to be in the gas phase which represents a "worst case" situation.

Again, the operating conditions reported do not represent optimum scrubber designs and are merely for comparative purposes. Other scrubbing processes will differ in the operating conditions required to obtain the same

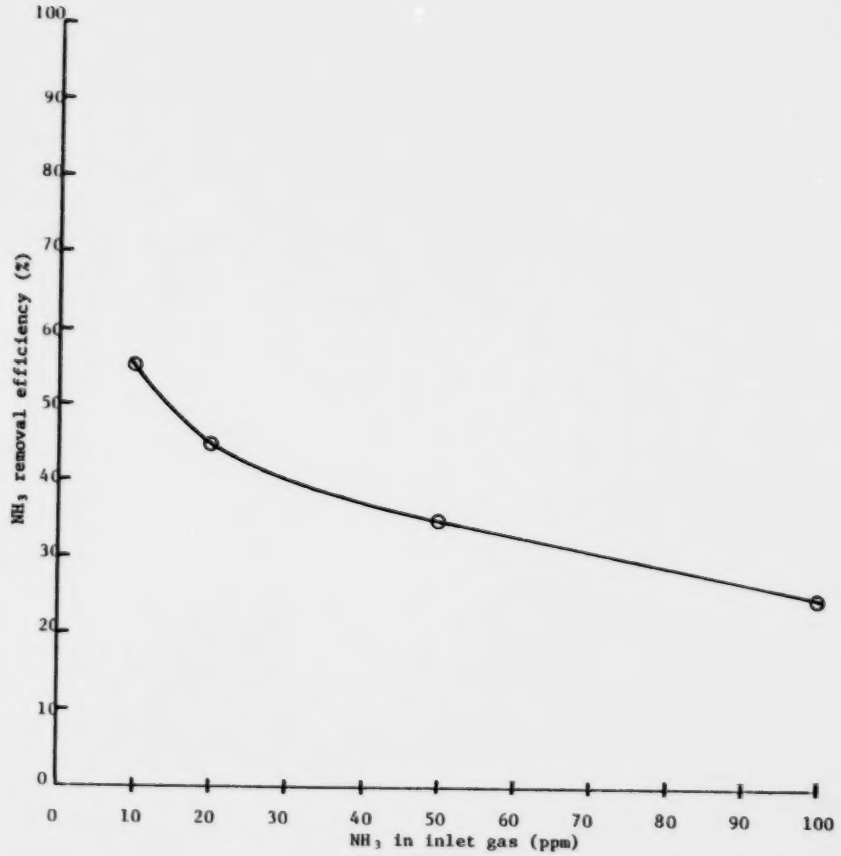


Figure 4-4. Calculated NH_3 removal efficiency (steady-state) in limestone scrubber vs NH_3(g) in inlet gas (Western coal).

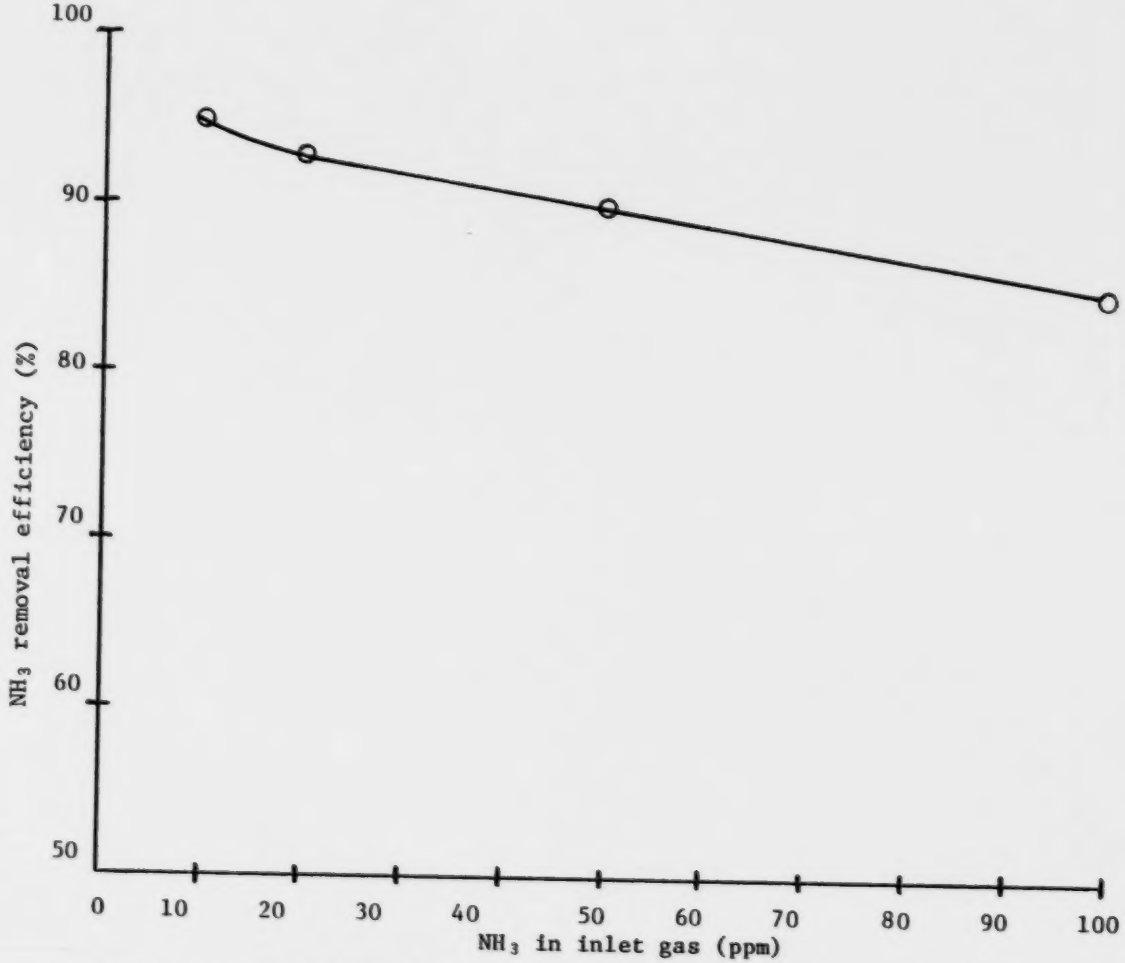


Figure 4-5. Calculated NH_3 removal efficiency (steady-state) in limestone scrubber vs NH_3(g) in inlet gas (Eastern coal).

SO_2 removal. However, with respect to SO_2 removal, the effects of absorbed ammonia on other wet FGD processes should be similar to those calculated for a limestone scrubbing system. The magnitude of the effects will depend on the amount of ammonia absorbed. As discussed in Section 4.1, other FGD processes typically operate at higher pH levels than limestone processes and therefore should absorb less ammonia. Processing the ammonia-contaminated liquor is discussed for the other FGD systems in Section 4.3.

4.2.1 SO_2 Removal

In general terms, the rate of SO_2 sorption in an FGD system can be correlated with the following design equation:

$$R_{SO_2} = K_G \cdot a \cdot V \cdot \ell m\left(P_{SO_2} - P^*_{SO_2}\right) \qquad (4\text{-}1)$$

where:

R_{SO_2} = molar rate of SO_2 sorption,

K_G = overall gas/liquid mass transfer coefficient,

a = gas/liquid interfacial area per unit volume of scrubber

V = scrubber volume

$\ell m\left(P_{SO_2} - P^*_{SO_2}\right)$ = log mean driving force between SO_2 partial pressure in the flue gas $\left(P_{SO_2}\right)$ and the equilibrium SO_2 partial pressure of the scrubber liquor $\left(P^*_{SO_2}\right)$.

SO_2 absorption is encouraged by maintaining a sufficient driving force $\left(P_{SO_2} - P^*_{SO_2}\right)$ and by providing sufficient gas-liquid mass transfer area (a) in the scrubber. The driving force term is governed by the process chemistry and liquid-to-gas ratio (L/G) while the interfacial area is affected by both contactor design and L/G.

The overall mass transfer coefficient, K_G is influenced by a number of variables. Equation 4-2 shows the normal definition of K_G:

$$K_G = \left(\frac{1}{k_g} + \frac{H}{k_\ell} \right)^{-1} \qquad (4\text{-}2)$$

where k_g and k_ℓ are the individual gas and liquid side mass transfer coefficients which describe the diffusion rate of a component across two typothetical stagnant films. H is Henry's equilibrium constant for a gas-liquid mixture. In certain situations encountered in FGD systems, either individual coefficient may be the one controlling overall mass-transfer. The principle example where mass transfer could be gas film limited is in the case of low inlet SO_2 concentrations. At low inlet SO_2 concentrations and high L/G ratios, increases in the inlet SO_2 concentrations can be experienced with no loss in scrubber removal efficiency.[36] The liquid phase alkalinity will also have a marked effect on mass transfer limitations. At higher SO_2 concentrations the liquid film resistance becomes more significant. The liquid phase resistance can be lowered by raising the concentration of liquid species which are alkaline with respect to SO_2 sorption.

Usually, a large portion of the alkalinity required for SO_2 removal is derived from solids dissolution in the scrubber, predominantly calcium sulfite and calcium carbonate. Because solid-liquid reactions tend to be significantly slower than liquid-liquid reactions, it is advantageous to minimize the amount of solids dissolution required by maximizing liquid phase alkalinity in the scrubber feed liquor. Since sorbed ammonia will increase the liquid phase alkalinity, it is theoretically possible to achieve the same SO_2 removal at lower L/G values. At some level of L/G reduction, however, two factors will prevent further reduction without accompanying decreases in the SO_2 removal. The interfacial contact area may become limiting as the liquid rate is reduced. Additionally, as k_ℓ increases, k_g becomes the limiting factor in the overall mass transfer coefficient.

Figures 4-6 and 4-7 present the L/G calculated using the RIPS model for typical Western and Eastern coal applications as a function of the inlet gas ammonia concentration for a constant 90 percent SO_2 removal. These plots show

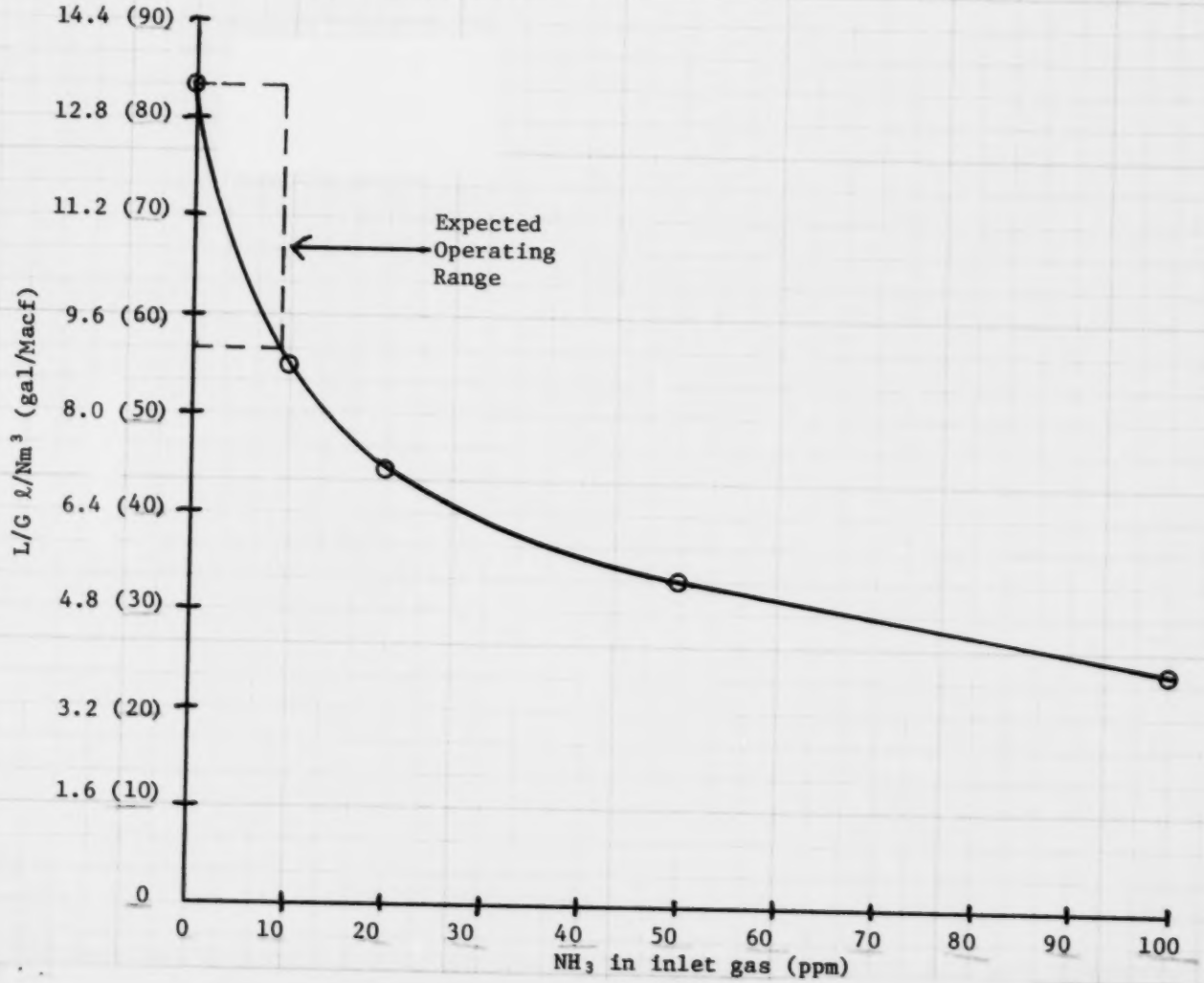


Figure 4-6. Required L/G (based on alkalinity) for SO_2 removal vs NH_3(g) in inlet gas (Western coal).

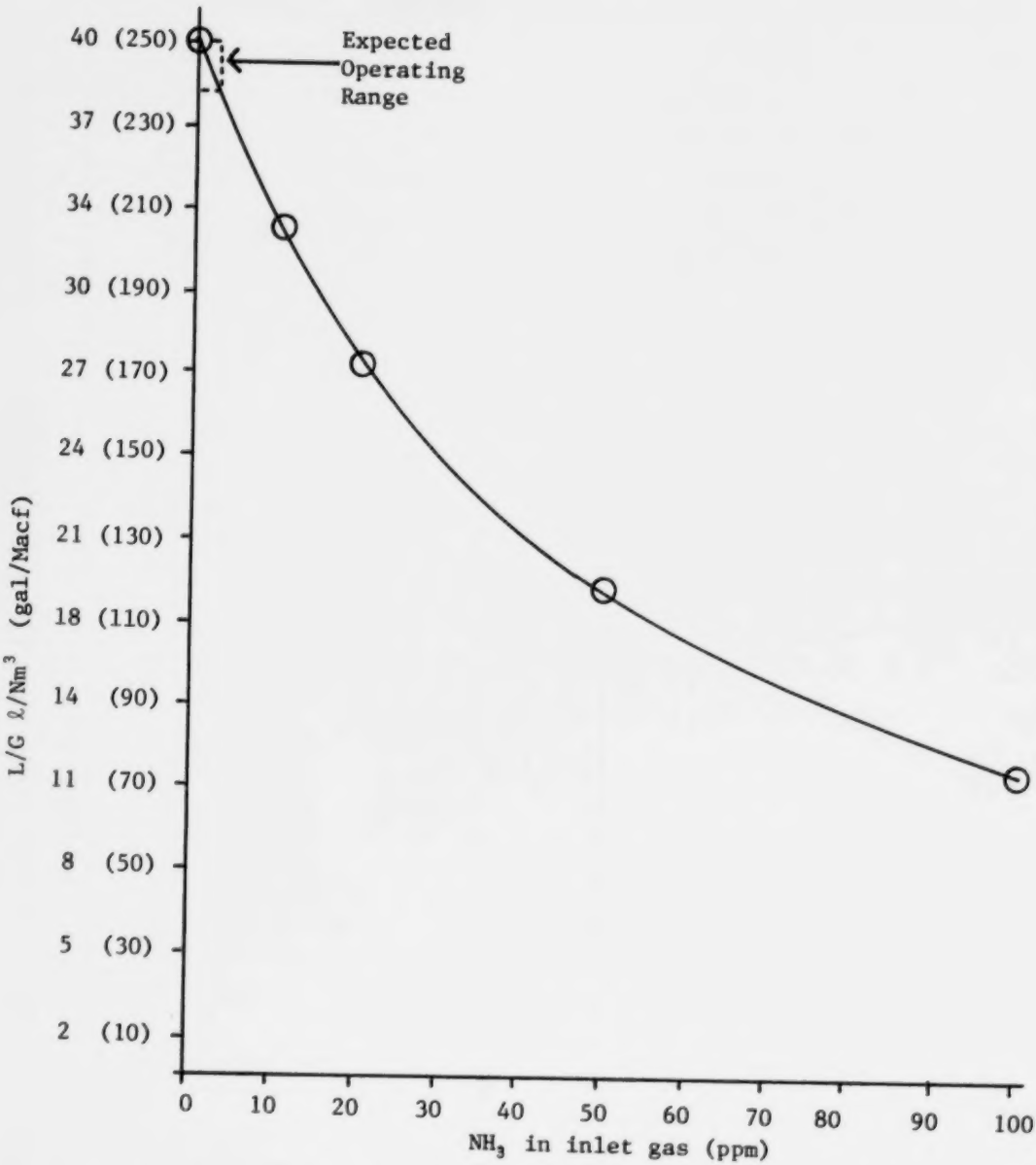


Figure 4-7. Required L/G (based on alkalinity) for 90 percent SO_2 removal vs NH_3(g) in inlet gas (Eastern coal).

that the L/G values required for both Eastern and Western coals drop as the inlet flue gas NH_3 concentration increases. This can also be seen in Table 4-5 which shows the effect of ammonia concentration in the scrubbing liquor on the required L/G. At the maximum NH_3 liquor concentrations, a 70 percent reduction in L/G was predicted for both coals. Such large reductions will probably not be achievable, however, since these ammonia concentrations will occur only when steady-state conditions are reached. High ammonia levels would be expected only during a process upset and would not be a steady-state condition.

In summary, ammonia absorbed from the flue gas should not present any problems for SO_2 removal. More liquid phase alkalinity will be available as the ammonia concentration in the scrubbing liquor increases. At expected inlet ammonia concentrations of 1-3 ppm, slightly lower L/G's or small increases in the SO_2 removal will probably be noted. Under upset conditions (50 ppm, 100 ppm), the SO_2 removal should increase noticeably. However, sludge ammonia concentrations will not reach the steady-state levels predicted by the computer simulations due to the transient nature of upset conditions. Regardless, from an SO_2 removal standpoint the FGD system should benefit from the presence of ammonia in the flue gas.

4.2.2 Scale Potential

In a limestone scrubbing process, the scrubbing liquor can be thought of as a medium for transferring sulfur species from the gas to the solid phase. Because sulfite is oxidized in the scrubber and both calcium sulfite and calcium sulfate are relatively insoluble, these species must be removed primarily as solid materials. Therefore, at steady-state, material balance considerations require that the SO_2 removal rate, the net sulfur species precipitation rate, and the solid sulfur species removal rate be effectively equal (on a molar flow basis). This material balance is indicated in Equation 4-3.

$$\begin{matrix}\text{SO}_2 \\ \text{removal rate}\end{matrix} = \begin{matrix}\text{Net sulfur species} \\ \text{precipitation rate}\end{matrix} = \begin{matrix}\text{Solid sulfur species} \\ \text{removal rate}\end{matrix} \qquad (4\text{-}3)$$

TABLE 4-5. EFFECT OF SCRUBBING LIQUOR AMMONIA CONCENTRATION ON THEORETICAL L/G REQUIRED FOR 90 PERCENT SO_2 REMOVAL

Run	Flue gas NH_3 concentration, ppm	Scrubbing liquor* NH_3 concentration, mg/ℓ	L/G, ℓ/Nm^3 (gal/Macf)**
Eastern coal			
1	100	3550	11.7 (73)
2	50	1887	18.4 (115)
3	20	783	27.6 (172)
4	10	400	33.0 (206)
5	0	0	39.9 (249)
Western coal			
1	100	6580	3.8 (24)
2	50	4615	5.3 (33)
3	20	2390	7.1 (44)
4	10	1466	8.7 (54)
5	0	0	13.3 (83)

*Based upon steady-state operation.

**Minimum value based on alkalinity requirements. Mass transfer area limitations may require larger L/G's in some of the Western coal cases.

The solid sulfur species formed are mainly calcium sulfite/sulfate coprecipitate [$(1-x)CaSO_3 \cdot xCaSO_4 \cdot \frac{1}{2}H_2O$] and gypsum ($CaSO_4 \cdot 2H_2O$). These are precipitated through the following reactions:

$$Ca^{++} + xSO_4^{=} + (1-x)SO_3^{=} + \tfrac{1}{2}H_2O \rightleftarrows (1-x)CaSO_3 \cdot xCaSO_4 \cdot \tfrac{1}{2}H_2O \downarrow \qquad (4\text{-}4)$$

$$Ca^{++} + SO_4^{=} + 2H_2O \rightleftarrows CaSO_4 \cdot 2H_2O \downarrow \qquad (4\text{-}5)$$

Essentially all of the precipitated sulfite and some of the precipitated sulfate are removed as coprecipitate. However, sulfite oxidations higher than approximately 15 to 16 percent require the precipitation of gypsum to meet material balance requirements.

The scaling phenomenon is best explained in terms of the relative saturations of precipitating species. The relative saturation (RS) of a precipitating material, $CaSO_4 \cdot 2H_2O$ for example, can be expressed as:

$$RS_{CaSO_4 \cdot 2H_2O} = \frac{a_{Ca^{++}}\, a_{SO_4^{=}}\, a^2_{H_2O}}{K_{SP_{CaSO_4 \cdot 2H_2O}}} \qquad (4\text{-}6)$$

where the "a" terms in Equation 4-6 are the activities of the subscripted species and K_{SP} is the solubility product constant of the precipitating material. The activity (a) of species is the product of activity coefficients (γ) and species concentration (m). The activity coefficient accounts for the non-ideal behavior of scrubbing solutions.

The precipitation of coprecipitate has been correlated with the relative saturation of calcium sulfite hemihydrate ($CaSO_3 \cdot \frac{1}{2}H_2O$). The precipitation rate of gypsum has been correlated with the relative saturation of calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$). A generalized plot of precipitation rate versus relative saturation is shown in Figure 4-8. At low relative saturations, both calcium sulfite/sulfate coprecipitate and calcium sulfate dihydrate precipitate through a crystal growth mechanism whereby these solids

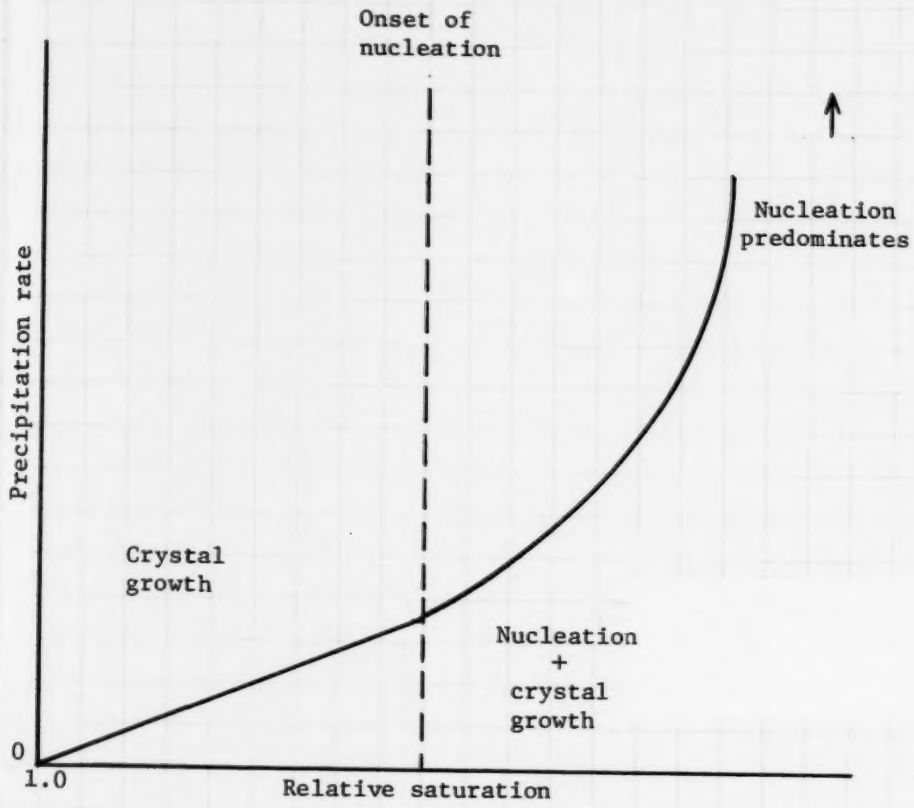


Figure 4-8. Precipitation rate effects as a function of relative saturation.

precipitate only upon existing seed crystals. In this region, precipitation is governed by a kinetic expression of the form shown in Equation 4-7.

$$R_P = k \cdot \alpha \cdot V \cdot C \cdot (RS-1) \qquad (4-7)$$

where R_P (gmoles/time) is the precipitation rate, k is a precipitation rate constant (gmoles/area-time-driving force), α is the seed crystal area per gram of solids, V is the volume of the system, C is the concentration of the precipitating solid species in grams per unit volume of slurry, and RS is the relative saturation of the precipitating material.

If the system is not designed properly or the system chemistry is not controlled properly, the relative saturation may reach a level at which precipitation will occur not only by the mechanism of crystal growth but also by nucleation. In the nucleating region, existing crystal growth sites become a limiting factor for the precipitation of solids causing new crystals to form spontaneously. The critical relative saturation value at which nucleation begins to occur is significant from a process control point of view because conditions which lead to nucleation also tend to promote scaling. For $CaSO_4 \cdot 2H_2O$, scaling conditions are usually associated with relative saturations above 1.3-1.4. The critical relative saturation value for calcium sulfite hemihydrate ($CaSO_3 \cdot \frac{1}{2}H_2O$) is not as well defined, but is known to be at least three to four times greater.

A reasonable way to assure that nonscaling conditions are maintained is to control the relative saturations of both calcium sulfite and calcium sulfate below their critical nucleation thresholds. This is particularly important at key system locations such as pump suction lines and certain portions of the scrubber internals.

Calcium sulfite/sulfate coprecipitate scaling is usually not as critical as gypsum scaling. Coprecipitate scale is softer and can usually be removed by lowering the system pH.

For the process simulations run in this study, the reaction tank volume required to maintain a scrubber bottoms gypsum relative saturation of 1.3 was calculated. As shown in Figures 4-9 and 4-10, the required reaction volume increases initially reaching a maximum of approximately 2.12×10^6 ℓ (560,000 gals) for the Western coal and 6.66×10^6 ℓ (1,760,000 gals) for the Eastern coal. This initial rise in tank volume is then followed by a decrease as the ammonia concentration becomes greater. The initial increase in tank volume is caused by the reduction in the L/G required to maintain the SO_2 removal. Lowering the L/G means that more SO_2 is picked up per unit volume of scrubbing liquor. This results in greater increases in the relative saturation across the scrubber (for a fixed sulfite oxidation). At higher ammonia levels, the increased pickup and oxidation of SO_2 per liquor volume is offset by the higher ammonia concentrations, which complex with the free $SO_4^{=}$.

At the expected gaseous ammonia concentrations of 1-3 ppm, a slight increase in SO_2 removal would be expected at the same L/G. This increase would probably be accepted rather than adjusting the L/G to maintain a constant SO_2 removal. The possibility of scaling would be dealt with by increasing the recirculating percent solids rather than increasing the reaction tank volume. Higher ammonia levels, such as those simulated, would only be expected under transient conditions. These occurrences would not significantly change the steady-state ammonia liquid concentrations because of the large residence time of most FGD systems.

4.2.3 Solids Dissolution and Precipitation

As shown in Equation 4-3, the SO_2 removed from the flue gas must be purged from a limestone scrubbing system as solid $CaSO_3/CaSO_4$ coprecipitate and $CaSO_4 \cdot 2H_2O$. However, a small amount of sulfur exits the system in the liquid that accompanies the solid sulfur species. In the presence of ammonia, the amount of sulfur present in the liquid phase will increase. This was shown in Tables 4-3 and 4-4 where the concentrations of both $SO_3^{=}$ and $SO_4^{=}$ increased as the ammonia level increased.

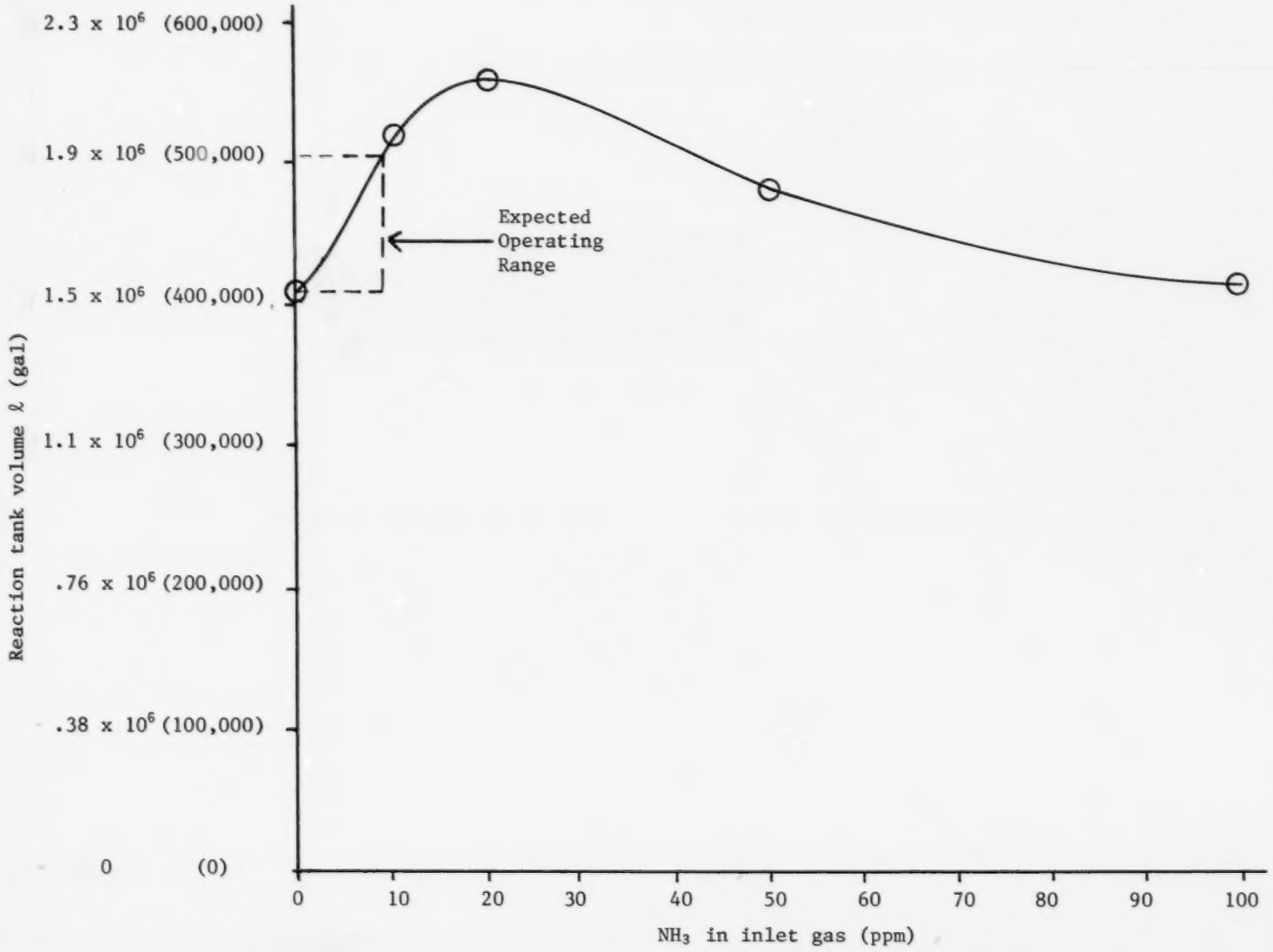


Figure 4-9. Required reaction tank volume to prevent scaling vs $NH_3(g)$ in inlet gas (Western coal).

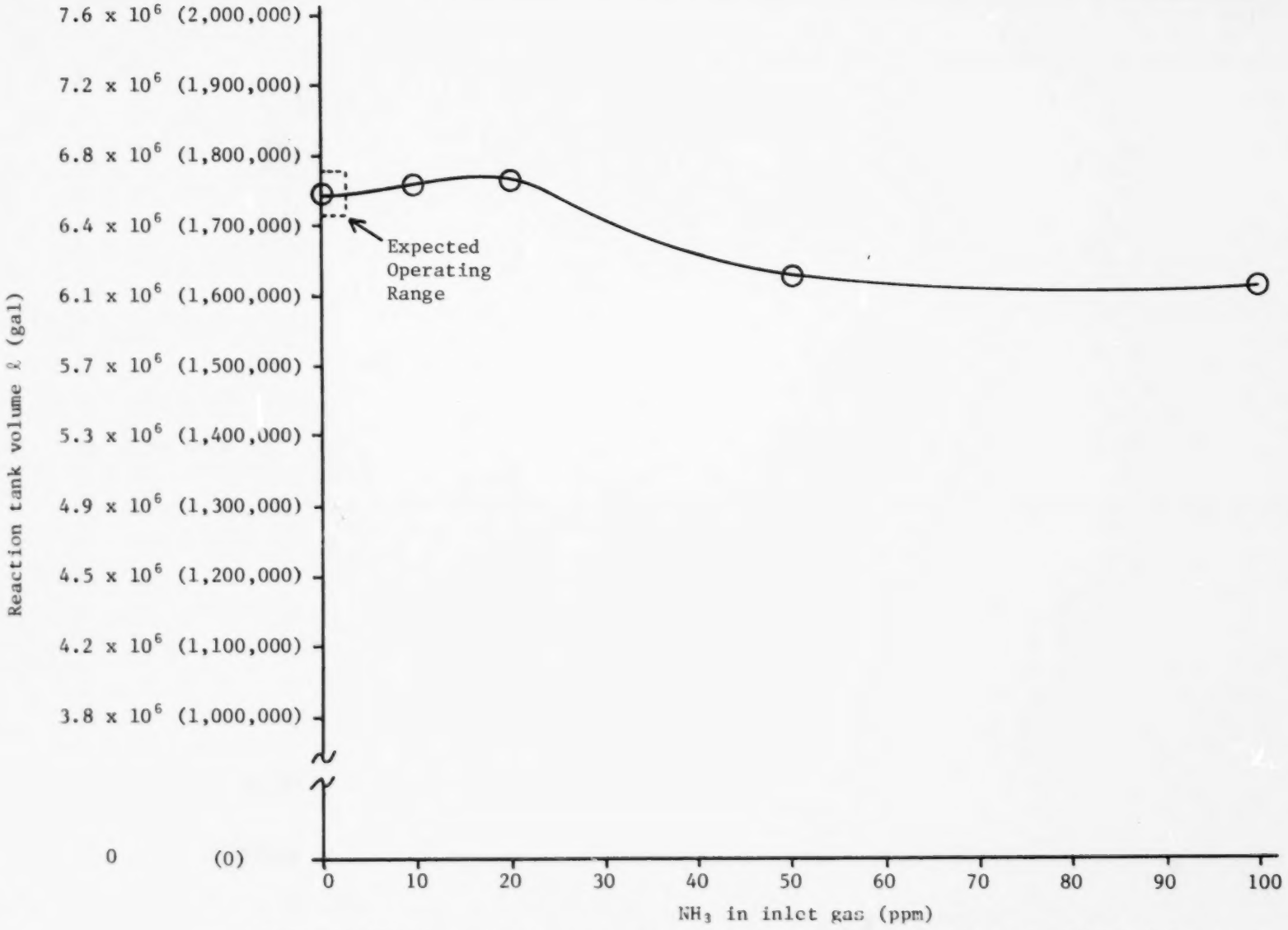


Figure 4-10. Required reaction tank volume to prevent scaling vs NH_3(g) in inlet gas (Eastern coal).

Tables 4-6 and 4-7 show the effect of ammonia on the precipitation rates of $CaSO_3/SO_4 \cdot \frac{1}{2}H_2O$ coprecipitate and $CaSO_4 \cdot 2H_2O$. At the maximum levels, the total rate of precipitation of the sulfur species decreased by 3.6 percent for the Eastern coal and 2.8 percent for the Western coal. These lower precipitation rates are also reflected in an increase in the total sulfur in the liquid phase.

The amount of calcium in solution is lower at high inlet ammonia concentrations since more $CaCO_3$ is present in the solid phase. As shown in Tables 4-6 and 4-7 the solid phase $CaCO_3$ in the sludge increased by 63 percent for the Western coal and 21 percent for the Eastern coal at the maximum ammonia concentrations. Again, these high ammonia levels would only be expected for short periods of time under upset conditions. Therefore, ammonia concentrations will not have sufficient time to approach the steady state concentrations shown here. However, the important point is that when ammonia is introduced to the FGD system, less $CaCO_3(s)$ is required to meet the alkalinity requirements of the system. Thus, slightly lower stoichiometries may be possible to reduce the amount of the excess $CaCO_3(s)$ which is exiting with the sludge and not being utilized in the system.

No investigation was undertaken to examine the effect of ammonia on sludge handling properties or crystal morphology. However, systems which produce a marketable by-product (such as gypsum) may not be able to accept ammonia impurities in the sludge.

4.3 OTHER FGD SYSTEMS

The impact of ammonia on other FGD systems should also be beneficial with respect to SO_2 removal because of the additional liquid phase alkalinity. Lime, magnesium, and sodium-based systems will probably remove less ammonia than limestone because of their higher operating pH's. The lower operating pH systems (such as the Chiyoda Thoroughbred 121) will remove greater amounts of ammonia. For the throwaway FGD systems, ammonia contamination in the sludge may not be a serious processing problem. If by-product recovery is

TABLE 4-6. SUMMARY OF EFFECTS OF AMMONIA ON SOLIDS DISSOLUTION AND PRECIPITATION IN LIMESTONE FGD SYSTEMS (WESTERN COAL)

Run #	Flue Gas Inlet NH_3 (ppm)	Sludge Liquid NH_3 (mg/ℓ)	Precipitation rates (gmoles/sec)		Sludge flow rates (gmoles/sec)				S leaving system	
			$CaSO_3/SO_4$ Coprecipitate	$CaSO_4 \cdot 2H_2O$	NH_xSO_x	Liq phase S	Solid phase S	$CaCO_3$(s)	% Liq phase	% as NH_xSO_x
1	100	6580	1.02	8.56	.0360	.0845	9.75	.88	.86	.37
2	50	4615	1.09	8.60	.0136	.0442	9.79	.78	.45	.14
3	20	2390	1.10	8.63	.004	.0266	9.81	.66	.27	.04
4	10	1466	1.12	8.68	.002	.0229	9.82	.62	.23	.02
5	0	0	1.14	8.72	-	.0189	9.82	.54	.19	0

TABLE 4-7. SUMMARY OF EFFECTS OF AMMONIA ON SOLIDS DISSOLUTION AND PRECIPITATION IN LIMESTONE FGD SYSTEMS (EASTERN COAL)

Run #	Flue Gas Inlet NH_3 (ppm)	Sludge Liquid NH_3 (mg/ℓ)	Precipitation rates (gmoles/sec)		Sludge flow rates (gmoles/sec)				S leaving system	
			$CaSO_3/SO_4$ Coprecipitate	$CaSO_4 \cdot 2H_2O$	NH_xSO_x	Liq phase S	Solid phase S	$CaCO_3$(s)	% Liq phase	% as NH_xSO_x
1	100	3550	56.1	8.05	.178	.454	65.38	5.94	.69	.27
2	50	1887	57.2	8.08	.0477	.209	65.63	5.46	.32	.07
3	20	783	57.7	8.15	.0130	.141	65.70	5.14	.21	.02
4	10	400	58.0	8.19	.0059	.127	65.71	5.03	.19	.009
5	0	-	58.3	8.23		.116	65.73	4.91	.18	

practiced, the ammonia may present a problem, depending on the by-product use. For example, if gypsum is produced for agricultural use, ammonia is a valuable addition. If gypsum is used for wallboard or cement manufacturing, ammonia contamination could probably not be tolerated.

Regenerable FGD systems may require a purification step to remove ammonia prior to the SO_2 processing. For example, both the Welman-Lord and Citrate processes generate a highly concentrated SO_2 gas which can be processed to make sulfuric acid, elemental sulfur, or liquified SO_2. Any ammonia present in this gas stream will have to be removed in order to maintain product purity. This could be accomplished by using an ammonia absorber. The absorber liquor could then be reinjected into the flue gas, recycling the ammonia for NO_x control.

Spray dryers should not be affected by ammonia because no liquid recycle is involved. However, if solids recycle is employed the ammonia concentration in the scrubber feed slurry could increase. The disposal method of the collected solids will determine the amount of ammonia emissions.

The impact of ammonia compounds on corrosion in the FGD system is expected to be minimal. Ammonia does not significantly corrode stainless steels or the linings generally used. The major metals attacked by ammonia are copper and bronze alloys. The primary use of copper has been as fins on steam reheat tubes. Exposure tests would have to be conducted to determine the degree of corrosion in an actual system.

SECTION 5

HEALTH AND ENVIRONMENTAL EFFECTS

This section discusses the potential environmental and health effects associated with excess ammonia from a NO_x SCR process. Potential ammonia emissions may be in gaseous, liquid and/or particulate forms. The following sections discuss the potential quantities of each form of emission from electrostatic precipitators (ESP), baghouses, and flue gas desulfurization (FGD) systems, and the potential effects of these emissions.

5.1 GASEOUS AND PARTICULATE EMISSIONS

Gaseous ammonia emissions may result not only from ammonia passing through a particulate removal (ESP or baghouse) or FGD system and leaving with the stack gases, but also may be evolved from ash ponds and FGD sludge disposal ponds. The emission of ammonium sulfate/bisulfate particulates could occur due to poor particulate control equipment efficiency. An ammonium bisulfite plume could possibly form during upset conditions. First, the potential source and quantities of gaseous and particulate ammonia emissions will be discussed, followed by a discussion of the effects of these emissions.

5.1.1 Sources

The discussion in Section 3 concerning the ultimate fate of ammonia species entering an ESP system showed that for flue gas ammonia levels of 10-20 ppm exiting the SCR, 90 percent or more of the ammonia will be collected with the fly ash as ammonia salts. Only 1-3 ppm NH_3 will be present in the stack gases under these conditions with no additional flue gas cleanup down-

stream of the ESP. Estimates for baghouse emissions indicate even lower ammonia levels in the stack gases.

If the fly ash from the ESP or baghouse is handled entirely in the dry form, evolution of ammonia vapors from the solids would be extremely slow and not a significant source of ammonia. Table 5-1 shows the equilibrium partial pressure of ammonia ($P^*_{NH_3}$) over the predominant ammonium sulfate salts. As the temperature decreases, $P^*_{NH_3}$ decreases from 5-17 ppm at 200°C to 0.04-0.16 ppm at 120°C. These vapor pressures are small and should not result in any significant gaseous ammonia emissions.

TABLE 5-1. EQUILIBRIUM VAPOR PRESSURE OF AMMONIA OVER AMMONIUM SALTS

Temperature °C	$P^*_{NH_3}$ over $(NH_4)_2SO_4(s)$		$P^*_{NH_3}$ over $NH_4HSO_4(s)$	
	atm	ppm	atm	ppm
120	4.40×10^{-8}	0.040	1.58×10^{-7}	0.158
144	3.32×10^{-7}	0.332	1.26×10^{-6}	1.26
175	3.28×10^{-6}	3.28	1.27×10^{-5}	12.7
200	1.67×10^{-5}	16.7	5.33×10^{-5}	53.3
225	7.22×10^{-5}	72.2	2.17×10^{-4}	217.
300	2.72×10^{-3}	2720.	6.98×10^{-4}	698.

Reference 7

If the fly ash is sluiced to a settling pond, the potential for gaseous ammonia emissions is much greater. Fly ash slurries may be very basic to slightly acidic with pH values of 5-11. Calculated data presented in Section 3 (Table 3-3) show that for 10-20 ppm ammonia in the flue gas exiting the SCR and entering the ESP, 0.05-0.20 percent of the ash will be ammonia (0.05-0.10 percent for Eastern coal and 0.10-0.20 percent for Western coal). The ammonia will most likely be present in the ash as very soluble ammonia salts, which will rapidly dissolve when the ash is sluiced. The pH of the fly ash slurry will determine the potential for gaseous ammonia to be evolved. As pH increases, the ammonia equilibrium vapor pressure increases and the potential

for ammonia evolution is increased. Table 5-2 presents the ammonia vapor pressure for the Eastern and Western case sludge liquor compositions with 10 ppm NH_3 in the flue gas. The liquid ammonia concentration reached is comparable to that obtained by combining the FGD and fly ash wastes or sluicing the fly ash separately. As can be seen, if the fly ash is alkaline, ammonia will evolve from the pond. The vapor pressure is strongly affected by both pH and ammonia concentration. The liquid composition (other than ammonia) only moderately affects the vapor pressure. In the Eastern case, the ammonia concentration is 400 mg/ℓ as opposed to 1466 mg/ℓ for the Western coal. The ratio between vapor pressure and liquid ammonia concentration at a constant pH is linear over the range shown here.

TABLE 5-2. NH_3 VAPOR PRESSURE AS A FUNCTION OF pH[1] FOR FGD SLUDGE LIQUOR pH

pH	$P^*_{NH_3}$ (ppm)	
	Eastern Coal	Western Coal
6	0.04	0.14
7	0.43	1.4
8	4.2	14.
9	36.	130
10	150	570

[1]Using liquid composition of Case 4, Tables 4-3 and 4-4 (10 ppm NH_3 inlet to FGD system, liquid NH_3 concentrations, Eastern - 400 mg/ℓ, Western - 1466 mg/ℓ at 16°C).

The discussions in Section 4 concerning the ultimate fate of ammonia species entering an FGD system show that the removal of gaseous ammonia can vary significantly with coal sulfur content. For a low sulfur Western coal with limestone scrubbing, about 50 percent of the gaseous ammonia entering the FGD system will be absorbed by the scrubbing liquor. However, for the same situation applied to a high sulfur Eastern coal, about 95 percent of the inlet gaseous ammonia will be absorbed. Stack emissions should be less than 1 ppm when a FGD system is used in conjunction with an ESP or baghouse

for gaseous ammonia levels of 10-20 ppm in the exit SCR gas. This assumes typical ammonia salt formation rates and removals by the particulate control equipment.

There are two types of ammonia plumes which could possibly exist, although the occurrence of either is seldom seen in Japanese installations. One cause of a visible plume is ammonium bisulfate and sulfate particulates. The other is ammonium bisulfite. As discussed in the previous sections, the ammonium bisulfate and sulfate salts should be effectively controlled by the ESP or baghouse. The only configuration where sulfate/bisulfate salts may not be removed is if a hotside ESP is used. In this case, the FGD system would probably not effectively control the submicron particles, possibly resulting in a visible plume. Additionally, plumes due to ammonium chloride have been reported when gaseous chloride levels exceed 10 ppm. [37,38]

The other cause of a visible plume is ammonium bisulfite which is produced by the reaction of gaseous NH_3, SO_2, and water. Figure 6-1 shows the point at which ammonium bisulfite plume formation would be expected. Based upon this data, plume formation would be predicted for gaseous ammonia concentrations of 5-10 ppm at the stack at a temperature of approximately 20°C. Since stack gases can cool rapidly to ambient temperatures and still maintain their concentration, a detached plume could result from the bisulfite particles. Table 5-3 shows plume formation temperatures for various SO_2 and NH_3 concentrations. One method proposed to eliminate bisulfite plume formation involves using an acidic wash of the flue gas followed by efficient mist elimination.[38] According to the cited reference, reheat was not required to prevent an ammonium bisulfite plume. Mesh mist eliminators were used in the test program.

In any process using large quantities of ammonia, some leakage from the process equipment, from the venting of tanks, and from spills during transfer must be expected. With reasonable equipment design and maintenance, such leaks should represent only a very small part of total process usage, and so

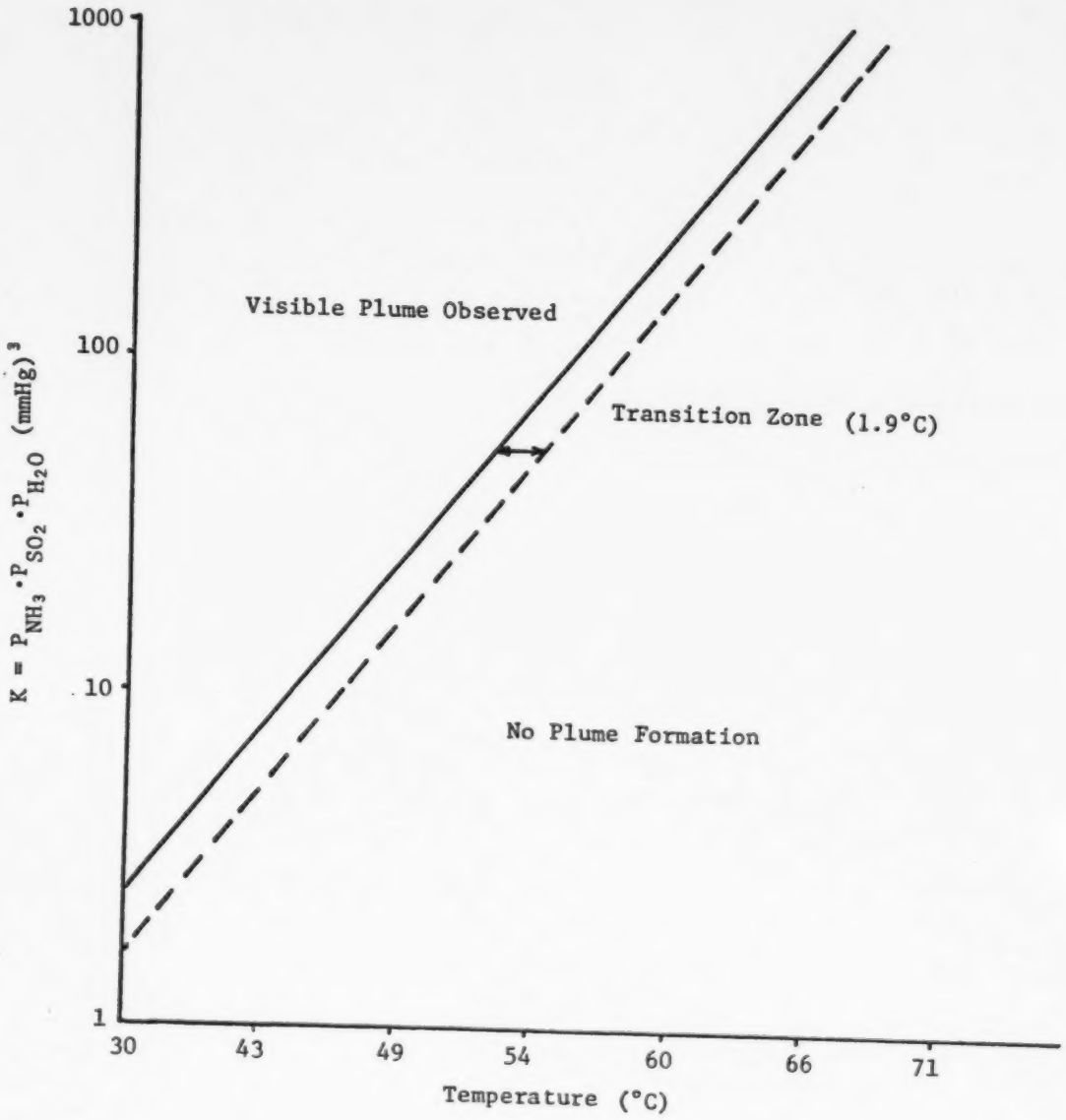


Figure 5-1. Ammonium bisulfite plume avoidance criteria.

Source: 38

TABLE 5-3. AMMONIUM BISULFITE PLUME FORMATION TEMPERATURES

Stack Concentration[1]		Ammonium Bisulfite Plume Formation Temperature
SO_2 (ppm)	NH_3 (ppm)	(C°)
300	100	37
	10	27
	1	18
	0.1	9
	0.01	2
120	100	33
	10	23
	1	14
	0.1	6
	0.01	-2
40	100	28
	10	19
	1	11
	0.1	2
	0.01	-5

[1]Moisture - 14 percent by volume.

Source: Equation presented in reference 38.

would not pose any special hazard except perhaps to workers in the immediate vicinity of the leaks.

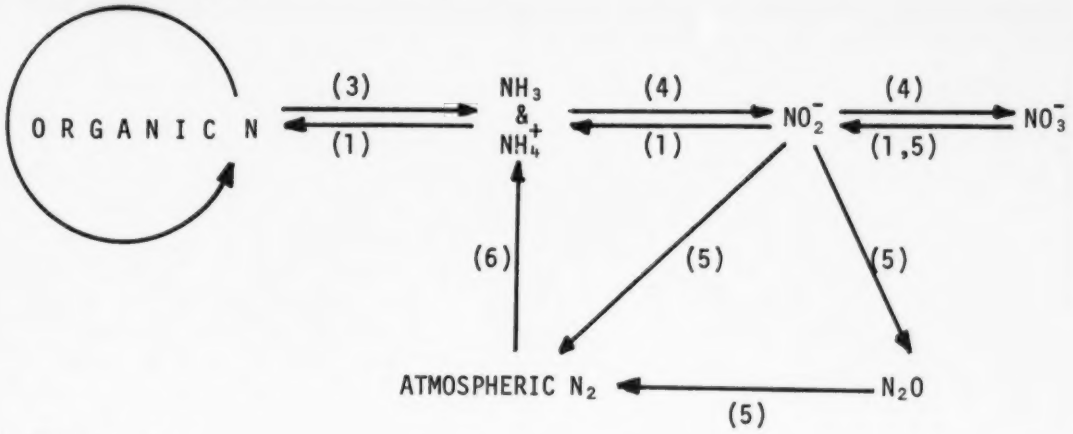
If ammonia is to be stored on-site in any large quantity, the possibility of a major accident exists. Ammonia is usually shipped and stored in liquid anhydrous form or as a strong (18-30 percent) aqueous solution. Any large leaks from rail cars, pipelines, barges, recirculation pumps, or storate tanks would pose a significant hazard.

5.1.2 Effects

The health and environmental effects of gasious ammonia may be loosely categorized according to the concentrations involved. Low exposure is considered to be less than 1 ppm. Medium exposure is that under the daily Threshold Limit Value (TLV), and high exposure is exposure to concentrations significantly higher than the TLV. The OSHA Permissable Exposure Limit for NH_3 is 50 ppm which is higher than would be expected to occur during normal operation of the SCR system.

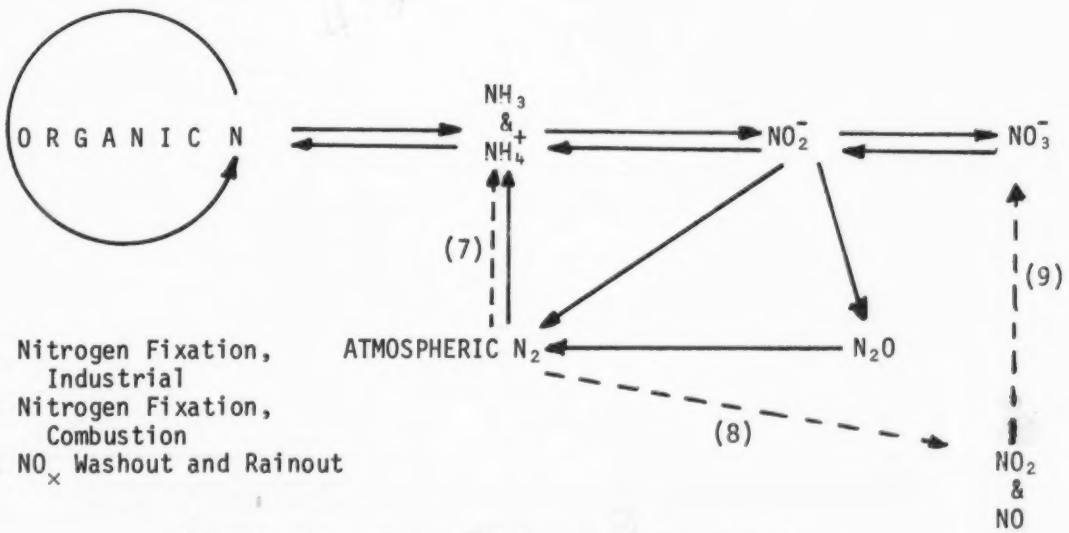
The effect of low concentrations on the environment around the plant should be minimal. Although ammonia only occurs naturally at concentrations of a few parts per billion, it is an important intermediate in protein metabolism and the global nitrogen cycle. Figure 5-2 shows that ammonia is an intermediate in three nitrogen routes: biologic fixation, assimilation of nitrates, and the ammonification/nitrification route to nitrates. Because ammonia takes part in so many biologic processes it has a short half-life in the atmosphere. In contrast to the nitrogen oxides, no adverse environmental effects have been shown for ammonia concentrations below 1 ppm.[39,40,41]

Both man-made ammonia and the nitrogen oxides introduce new routes in the global nitrogen cycle (Figure 5-3). Industrial ammonia manufacture may increase global nitrogen fixation by 40 percent.[39] Energy considerations normally favor the formation of nitrogen gas over the formation of nitrates, hence the atmospheric nitrogen pool is many orders of magnitude greater than the nitrate pool available to the biosphere. Because of this, nitrates tend



1. Assimilation
2. Heterotrophic Conversion
3. Ammonification
4. Nitrification
5. Denitrification
6. Nitrogen Fixation, Biologic

Figure 5-2. Simplifed biologic nitrogen cycle.



7. Nitrogen Fixation, Industrial
8. Nitrogen Fixation, Combustion
9. NO_x Washout and Rainout

Figure 5-3. Human effects on nitrogen cycle.

to be one of the limiting nutrients in the biosphere, and increases in nitrate levels have caused serious eutrophication problems in some areas.[39,42] But the overall effect of NO_x SCR control is to reduce the NO_x emissions substantially with a much smaller increase in ammonia emissions.

The effect on humans outside the battery limits of exposure to low level ammonia should be neglible. Ammonia has not been identified as a carcinogen,[39,43] and no adverse health effects have been documented for exposure under 1 ppm, for human or test animals.[39,43,44] In most humans, ingested ammonia is rapidly metabolized.[39]

The Threshold Limit Value (TLV) for occupational exposure to ammonia is an 8-hour time-weighted-average of 25 ppm, with a recommended ceiling of 35 ppm.[45] These values were chosen largely on the basis of surveys of workers exposed to ammonia, who reported little irritation at concentrations of 50 ppm or below.[43]

Experiments on animals have generally shown little damage from continuous exposure to concentrations below 100 ppm, except that test animals are much more sensitive to infectious lung diseases. Chickens and rats exposed to 20 to 25 ppm had significantly higher infection rates than controls.[39] The NIOSH criteria document for ammonia[43] and one survey of the field[39] recommend that a careful epidemiologic survey is needed to determine possible hazards of occupational exposure. All of this suggests that, while the 25 ppm TLV is apparently safe, epidemiologic surveys and animal infectivity studies may lead to a lower TLV.

In a plant using a NO_x SCR system, worker exposure to ammonia may result from leaks in ammonia handling equipment, ammonia vapors over the fly ash pond or FGD sludge disposal pond. There is no reason to expect that careful equipment design, maintenance, and good ventilation cannot prevent excessive chronic exposure to ammonia from ammonia handling equipment and sludge and fly ash equipment. However, ammonia vapors over fly ash and FGD sludge ponds could be a problem and should be further evaluated.

If ammonia is to be stored inside the battery limits in concentrated form, the danger of accidental spills and equipment failure must be examined. The risks may be divided into two categories: short-term human health effects of high ammonia concentrations, and the ammonia's effect on the environment outside the battery limits.

Ammonia is very toxic to humans, and there is a real danger to people nearby if an accident should occur that released any large quantity of ammonia. Concentrations of ammonia above 5,000 ppm (0.5 percent) are capable of causing blindness, lung damage, or death very rapidly.[39,43,44] It is important that plant personnel and nearby residents be informed of the proper safety and evacuation procedures in case of a spill.

The federal government has published a guide for short-term exposures of the public to ammonia, listing permissible exposures in the case of foreseeable, repeated releases and for the case of unforeseeable accidents.[46] Table 5-4 shows these limits.

Ammonia is readily absorbed by plants, and the danger to surrounding forests and agriculture would be severe if an ammonia plume were to form downwind of a spill or if unusual weather conditions caused extremely high ammonia concentrations. Studies on plants have shown that severe damage can be caused by only 3 to 12 ppm ammonia in 4 hours; 50 ppm in 1 hour; or by 1,000 ppm in a few minutes.[39,40]

Ammonia is very soluble in water, and at least one study has suggested that most of an ammonia plume could be absorbed by a large body of water.[47] The toxic effects of this ammonia probably would not be severe if the water were deep or flowing rapidly, because the cumulative concentration of ammonia would still be small. Ammonia's toxicity in water is strongly affected by pH and temperature as shown in Table 5-5.

TABLE 5-4. GUIDES FOR SHORT-TERM EXPOSURE OF THE PUBLIC TO AMMONIA

Short-Term Public Limits (STPL's)

10 min	20 ppm (ceiling)
30 min	10 ppm (ceiling)
60 min	10 ppm (ceiling)
5 hrs/day, 3-4 days/mo	5 ppm (time-weighted averages with excursions above average not to exceed "ceiling" limits)

Short-term public exposures are those occurring at predictable times and arising from single, or occasionally, repeated events. Since the exposure can be predicted there is no justification for submitting the public to any appreciable risk. The concentrations given above may be odorous, but are expected to be tolerable. They are considered to be below the level of irritation and well below the levels that might be expected to cause injury.

Many people find the odor of ammonia objectionable and any concentration above their odor threshold may be expected to produce complaints from these individuals regardless of how short the exposure.

Public Emergency Limits (PEL's)

10 min	100 ppm
30 min	75 ppm
60 min	50 ppm

Public emergency limits apply to situations in which ammonia escapes in an uncontrolled manner at unpredicted times and places as the result of accidents such as damage to transportation equipment or fire in a chemical-storage facility. Although the STPL's require that there be no adverse effects, the PEL's recognize the possibility of some serious discomfort, provided that the effect is reversible and that no serious sequelae result from it. The concentrations in the above PEL's are considered to present a strong odor with possible lacrimation and irritation of the upper respiratory tract (nose and throat), but no incapacitation or prevention of self-rescue.

Source: Ref. 46

TABLE 5-5. TOXICITY AND IONIZATION EXTENT OF AQUEOUS AMMONIA

Temp °C	pH 6.0	6.5	7.0	7.5	8.0	8.5	9.0
	Maximum Allowable Concentration, mg/ℓ (Un-ionized ammonia, %)						
5	160 (.0125)	51 (.0395)	16 (.175)	5.1 (.394)	1.6 (1.23)	0.53 (3.80)	0.18 (11.1)
10	110 (.0186)	34 (.0589)	11 (.186)	3.4 (.586)	1.1 (1.83)	0.36 (5.56)	0.13 (15.7)
15	73 (.0274)	23 (.0865)	7.3 (.273)	2.3 (.859)	0.75 (2.67)	0.25 (7.97)	0.093 (21.5)
20	50 (.0397)	16 (.125)	5.1 (.396)	1.6 (1.24)	0.52 (3.82)	0.18 (11.2)	0.070 (28.4)
25	35 (.0569)	11 (.180)	3.5 (.566)	1.1 (1.77)	0.37 (5.38)	0.13 (15.3)	0.055 (36.3)
30	25 (.0805)	7.9 (.254)	2.5 (.799)	0.81 (2.48)	0.27 (7.46)	0.099 (20.3)	0.045 (44.6)

Sources: Ref. 48,49.

As discussed in Section 3, ammonium sulfate and bisulfate particulates may form when the flue gas temperature drops, usually in the air preheater. These particulates are very fine (<0.2 microns), however 90-95 percent should be collected in the ESP and essentially all in a baghouse. The stack gases can be expected to contain less than 0.01 g/m of ammonium particulates. Ammonium sulfate and bisulfate are recognized as lung irritants,[50] but the concentrations at ground level due to a SCR system should be small.

Table 5-6 shows the irritant potency of ammonium sulfate and bisulfate aerosols in comparison to several other sulfate aerosols. These data represent laboratory tests on guinea pigs. Ammonium sulfate aerosols have been investigated for carcinogenic effects in combination with benzopyrene. An EPA-sponsored study concluded that ammonium sulfate is not a significant cause of cancer.[51]

TABLE 5-6. RELATIVE IRRITANT POTENCY OF SULFATES[1]

Sulfuric acid	100
Zinc ammonium sulfate	33
Ferric sulfate	26
Zinc sulfate	19
Ammonium sulfate	10
Ammonium bisulfate	3
Cupric sulfate	2
Ferrous sulfate	0.7
Sodium sulfate[2]	0.7
Manganous sulfate	-0.9

[1]0.3 μm particles, 300 to 9000 ng/m^3, based on comparison of increase in airway resistance.

[2]0.1 μm particles

Source: Ref. 50.

5.2 AQUEOUS EMISSIONS

Possible sources of aqueous ammonia emissions occur where fly ash and FGD sludges are handled and stored. Ash pond overflow and leachate from fly ash and FGD sludge disposal areas are the major potential sources of aqueous ammonia emissions resulting from the use of an upstream NO_x SCR system.

Data presented in Section 4 showed that 90+ percent of the ammonia entering the ESP will most likely leave the ESP as ammonium sulfate and bisulfate salts with the collected fly ash. These salts are very soluble and should dissolve completely when the fly ash is sluiced.

The ammonia concentration of ash pond overflow will depend on the level of ammonia entering the ESP, the ash content of the coal, the removal efficiency of the ESP, the amount of water used to sluice the ash from the ESP hoppers to the ash pond, and the pH of the ash pond liquor. The pH of the ash pond liquor will also influence the potential for the aqueous ammonia to evolve as gaseous ammonia. Higher pond pH levels will promote ammonia evolution.

As the ratio of ammonia in the flue gas to the ash in the flue gas increases (i.e., the ash content of the coal decreases) the potential aqueous ammonia concentration in the ash pond overflow increases. For example, assuming once-through fly ash sluicing at 5 percent solids and 10 ppm ammonia in the flue gas exiting the SCR, the maximum possible ammonia concentration in the ash pond overflow for the typical Eastern coal composition (16 percent ash) used in this study is about 30 mg/ℓ as NH_3.

For the typical Western coal composition (6.4 percent ash) used in this study, the maximum ammonia concentration in the ash pond overflow (based on the above assumptions) is about 60 mg/ℓ Although these concentrations are the maximum possible, actual concentrations may be significantly lower due to evolution of gaseous ammonia from the ash pond, especially if the ash pond liquor is basic (pH>7).

If FGD systems are designed with no aqueous discharges, the only potential for aqueous ammonia emissions is through FGD sludge pond leachate. Section 4 presented maximum FGD sludge liquor ammonia concentrations as a function of flue gas $NH_3(g)$ level. These concentrations ranged from 400 mg/ℓ for the Eastern coal application to 1470 mg/ℓ for the Western coal application when the FGD inlet flue gas $NH_3(g)$ concentration is 10 ppm. If most of the ammonia entering the FGD system is present as ammonium sulfate and bisulfate particulates, the sludge liquor ammonia concentration will depend on the removal of these fine particulates in the FGD system, which will be a function of the gas-liquid contactor type.

The EPA Water Quality Criteria for ammonia is 0.02 mg/ℓ, expressed as un-ionized ammonia.[49] Studies have shown that only the un-ionized form is toxic to aquatic life.[39,40,49,52] The extent of ionization is strongly dependent on pH and temperature, as shown in Table 5-5. If ash pond overflow or FGD leachate reaches ground waters or surface waters, treatment will be required to ensure that the ammonia quality criterion is met.

Fish appear to be the aquatic life most sensitive to ammonia. Studies have shown that the 96-hour 50 percent lethal concentration (96-hour LC_{50}) is as low as 0.20 mg/ℓ, expressed as total NH_3.[49,52] Lower concentrations can be expected to be hazardous over periods longer than 96 hours.

SECTION 6

ALTERNATIVES FOR OPERATION WITH AMMONIA LEAKAGE FROM NO_x SCR SYSTEMS

This section discusses the alternatives for preventing potential problems in ESP, baghouse, and FGD systems resulting from ammonia in flue gases exiting an NO_x SCR system. First, alternatives for potential problems directly associated with the ESP, baghouse, and FGD systems are discussed. Then, alternatives for potential problems resulting from ammonia-containing ash and FGD product disposal operations are discussed.

High levels of ammonia exiting the NO_x SCR system can occur from excessive ammonia feed rates or from reduced catalytic activity. Continuous analyses and indication of ammonia content of NO_x SCR outlet gas is needed. Excessive ammonia feed is correctable when detected by adjusting the ammonia feed rate controls. Low catalyst activity is correctable to some extent by increasing SCR temperature levels but eventually will require catalyst reactivation or replacement.

6.1 ESP SYSTEMS

As discussed in Section 3, one potential problem for ESP systems due to ammonia leakage from NO_x SCR systems is excessive adhesion of ash to ESP collector plates. This condition should only occur with fairly high gaseous NH_3 and SO_3 concentrations. Alternative actions to prevent this occurrence include using a hot side ESP system, closing monitoring and controlling NO_x SCR conditions, or accepting the excess ammonia and modifying collector plate cleaning procedures.

Use of a hotside ESP will avoid problems with the ESP system due to the SCR system. This may require a higher capital cost for the ESP but could also protect the NO_x SCR system and the air preheater from high concentrations of fly ash. Some low sulfur Western coal systems already use the hot (350°C) ESP designs to achieve economical and reliable particulate removal.[53,54] This is required because of excessive dust resistivity at preheater outlet temperatures (150°C). The high sulfur Eastern coal systems generally use the coldside ESP designs and obtain satisfactory performance.

A cold ESP with 99+ percent efficiency for particulate removal will cost about 16 million dollars for the standard 500 MW plant using high sulfur coal.[55] A hotside ESP for either Eastern or Western coal will cost about 25 million.[56] For a Western low sulfur coal which has very high resistivity ash at low temperatures, a coldside ESP could cost as much as 37 million.[55] It appears that the hotside ESP would cost less for some Western coals and possibly more for Eastern high sulfur coals compared to coldside ESP's.

One potential problem involved with hotside ESP's is increased sulfate deposits in downstream air preheaters. Electric Power Development Co. (EPDC) personnel in Japan report that when a hotside ESP upstream of the SCR unit was used during several tests on coal-fired power plant slipstreams, sulfate deposits forced an outage for preheater washing within seventeen days. In coldside ESP tests, soot blowing was sufficiently effective in controlling sulfate deposits in the air preheater such that washing would be required only once or twice a year. The reasons advanced by EPDC for this were that: (1) the fly ash abraded sulfate deposits on the preheater surface, and (2) some of the SO_3 and ammonium sulfate and bisulfate sorbed on the fly ash in the air preheater instead of depositing on the preheater.[1] A more comprehensive treatment of the effect of ammonia on air preheaters is considered under EPA Contract 68-02-2608, Task 68.[3] Japanese experience with ammonia contamination of ash has led some SCR operators to choose the hotside ESP upstream of the SCR system to prevent loss of ash sales and environmental problems in ash disposal.[1]

Two possible corrective actions for excessive adhesion to the ESP are (1) more intense or longer periods of rapping, or (2) washing of plates to clean them on either a continuous or intermittent basis. Literature from Australia noted that the dust adhesion was a problem only in older ESP systems which were known to have less rapping intensity than newer ESP's. The newer ESP systems did not exhibit this effect. Water washing of the plates about twice each month was used to overcome the problem with older ESP systems. The cost of upgrading rapper intensity would be relatively small provided an extended period (2 weeks) of boiler shutdown was previously scheduled, or if the upgrading were done when the NO_x SCR system was being installed. Converting an existing ESP from a dry to wet operating system may not be possible because of collecting electrode geometry. Periodic water washing would be a manual operation requiring a little capital investment but considerable labor and downtime.

6.2 BAGHOUSES

Little information is available on problems caused by ammonia in baghouses. However, several potential problems could exist. First, fly ash which contains ammonia could be sticky due to the hygroscopic nature of ammonia salts. Greater care will be required in cleaning and the cleaning frequency may have to be increased. The potential extent of irreversible impacts is not known. As a result, operating and maintenance costs could be higher. Fine ammonia particulates could also cause blinding by penetrating the bag fabric resulting in higher pressure drops. More frequent cleaning and possibly bag replacement may be required to maintain acceptable pressure drops.

The severity of these problems and corresponding costs are very difficult to evaluate based upon the limited data currently available. Further study should be performed before installing a SCR unit upstream of a baghouse. At present, it appears that the most viable system alternatives are to increase the cleaning frequency and carefully monitor pressure drop increases. Operating and bag replacement costs could potentially increase.

6.3 FGD SYSTEMS

As discussed in Section 5, no significant operating problems were identified for a limestone FGD system due to ammonia leakage from an upstream SCR unit at expected FGD inlet ammonia concentrations of 1-2 ppm. One possible benefit of ammonia in a FGD system is a slight increase in SO_2 removal or a decrease in the liquid-to-gas ratio (L/G) necessary to achieve the required SO_2 removal.

Ammonia particulates (i.e., $(NH_4)_2SO_4$, NH_4HSO_4) will probably not be removed in a low pressure drop scrubber. An upstream ESP or baghouse will remove these particulates. However, if a hotside ESP is used, ammonia particulates which pass through the scrubber may result in a visible plume. A more detailed discussion of the conditions which may result in plume formation was presented in Section 6.1. One method to control the ammonia particulate emissions is to use a fiber type mist eliminator after the scrubber mist eliminator. One facility reports excellent results using a Brinks type mist eliminator to remove ammonia salts from a sulfite boiler off gas which is scrubbed by an ammonia scrubber. Every three or four months the filters are removed and washed for 24 to 48 hours. Repacking is required about every two years.[57]

Retrofit facilities may not be able to handle the additional pressure drop, however, without the addition of a booster fan. This will increase both the capital and operating expenses. Assuming a 25-40 cm W.G. (10-16 in. W.G.) pressure drop across a Brinks type mist eliminator, additional fans should increase capital costs approximately $2.2/kW (for a 500 MW net capacity system) which represents about a 2 percent increase for both Eastern and Western coals.[58] Base case (0 ppm NH_3) capital costs (1979$) were estimated from TVA[59] and Pedco[60] data at $109/kW and $100/kW for an Eastern and Western coal, respectively.

Fan operating costs can vary between 0.20 and 0.26 mills/kW-hr depending upon the mist eliminator pressure drop. Lower pressure drops require more

filter elements. Therefore, there is an economic tradeoff between filter costs and fan operating costs. A Brinks type filter system at a pressure drop of 25 cm W.G. (10 in. W.G.) will require approximately 238 filter elements per scrubber module with a total cost (based upon four modules) of about $6.2/kW. At higher pressure drops (40 cm W.G.), the filter cost is reduced to about $4.7/kW with 182 filter elements per scrubber module. Filter tank costs should run about $200,000 per filter system. These estimates do not take into account any economy of size and are probably conservative. Prices are also for equipment costs only and do not include installation costs,[61] which will depend upon specific site arrangements but could be equal to or greater than the equipment costs.

Plume formation could also be a problem at the lower ammonia removals associated with the Western coal since gaseous ammonia can react with SO_2 in the stack gas and produce ammonium bisulfite particulates (see Section 6.1). A slightly observable plume has been reported at the Ogishima Ammonia Scrubbing Plant when outlet flue gas ammonia levels exceed 10 ppm.[62] Should excessive gaseous ammonia levels in the exit gas prove to be a problem, an acid wash prior to or after the scrubber may be required to reduce the $NH_3(g)$ emissions and plume formation.

In summary, ammonia does not appear to present any significant operational problems to an FGD system. FGD facilities with upstream ESP or baghouse systems should not experience any problems from the ammonia particulates. However, low pressure drop scrubbers with hotside ESP's may require the addition of a fiber type mist eliminator to remove the ammonia particulates and prevent visible plume formation. A booster fan may also be required to overcome the additional pressure drop in a retrofit system.

6.4 ASH AND FGD SYSTEM WASTE PRODUCT DISPOSAL OPERATIONS

The discussions presented in Section 5 showed that no significant gaseous or solid ammonia emissions should result from ammonia leaving a NO_x SCR system, but the potential for aqueous and secondary gaseous ammonia emissions exists for ash ponds and FGD sludge disposal ponds.

An alternative for preventing aqueous ammonia emissions in ash pond liquor discharge is to operate the fly ash sluice system in a closed loop (i.e., recycle ash pond overflow to sluice additional ash) or to use a portion of ash pond discharge elsewhere in the plant water system, such as make-up to an FGD system and recycle the remainder to sluice ash (partial closed-loop operation). The technical feasibility of closed-loop fly ash sluicing has not been demonstrated, although investigative studies have been performed with bench-scale equipment.[63] These studies, in conjunction with computer modeling calculations, showed that chemical treatment of recycled ash basin water may be required to prevent scaling and plugging in the ash sluice system. Furthermore, these studies showed that the level of treatment required, and therefore the cost of implementation, can vary significantly with ash composition. Some utility companies in Japan are using or planning to use biological treatment of waste water for ammonia removal when NO_x SCR systems are used.[1]

Worst case ash pond liquor and FGD sludge liquor ammonia concentrations were presented in Sections 3, 4 and 5 and these concentrations exceed the 0.02 mg/ℓ EPA Water Quality Criteria. However, the amount of ammonia which may reach groundwater due to leaching from ash and FGD sludge ponds is unknown. Laboratory studies are suggested to investigate leachate ammonia concentrations from ash and FGD sludge ponds as a function of liquor ammonia concentration and pH, and soil characteristics. The evolution of ammonia from the liquid is also a function of pH and ammonia concentration and needs further study to determine the severity of the problem.

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APPENDIX

PROCESS MODEL DESCRIPTION

This appendix describes the computational scheme or model used to estimate steady-state operating conditions for a typical FGD scrubbing process.

The important physical phenomena and process rate steps are formulated mathematically. Certain simplifying assumptions are made which lead to practical yet meaningful solutions describing the performance of the process.

The Radian process model is a group of computer programs for simulating aqueous inorganic chemical processes. The foundation of the model is the ability to predict vapor-liquid-solid mass transfer rates and chemical equilibrium for the CaO-MgO-Na_2O-SO_2-CO_2-SO_3-N_2O_5-HCl-P_2O_5-NH_3-H_2O system. The process model performs unit operation calculations and other engineering manipulations based upon (1) rate and equilibrium calculations and (2) process and equipment data which define the process flow scheme and characterize each of the individual process units.

The programs which make up the process model may be grouped into five major subdivisions: (1) rate and equilibrium calculation programs, (2) equipment subroutines which model each process unit and process input stream, (3) an executive system which interconnects the equipment subroutines to form an analog of the process flow diagram and controls the sequence of computer operations, (4) convergence routines which force convergence of the model iterative parameters, and (5) print routines which print out stream and process data.

PROCESS MODEL FLOW SHEET

A simple flow scheme is given in the symbology of the Radian process model as Figure A-1. This scheme was selected to simplify the model description so that the basic principles involved could be explained. Through the addition of solid-liquid separators, process "tees" and dividers, many process configurations may be simulated. Also, provisions can be used which account for pond evaporation and/or a liquid blowdown of known volume.

Subroutines FLUGS1, ALKINP, and WTRMKP simulate process inputs of flue gas, alkaline additive, and make-up water, respectively. Subroutine SCRUB5 models a spray tower and RATHLD simulates a stirred holding tank. Subroutines DIVDER and DIVDR3 simulate stream splitters, and FILTER models a clarifier-filter system. Subroutine SYSTB5 is an ancillary routine which performs material and energy balance calculations around the entire system.

Several assumptions have been incorporated into this simulation system.

1) The scrubber behaves as an adiabatic contacting device.

2) The partial pressures of CO_2 and H_2O in the gas leaving the scrubber are in equilibrium with the scrubber liquid at the scrubber temperature.

3) No precipitation occurs in the scrubber. However, dissolution of certain solid species such as $CaCO_3$ is allowed.

4) The temperature of the recirculating process liquor streams is fixed at the adiabatic saturation temperature of the scrubber effluent liquor.

5) The temperature of the make-up water has no effect upon the circulating liquor temperature.

6) Ionic reactions taking place in the liquid phase are rapid and thus are at equilibrium.

7) The holding time of the clarifier (modeled by the FILTER subroutine) is sufficiently long that solid-liquid equilibrium is achieved.

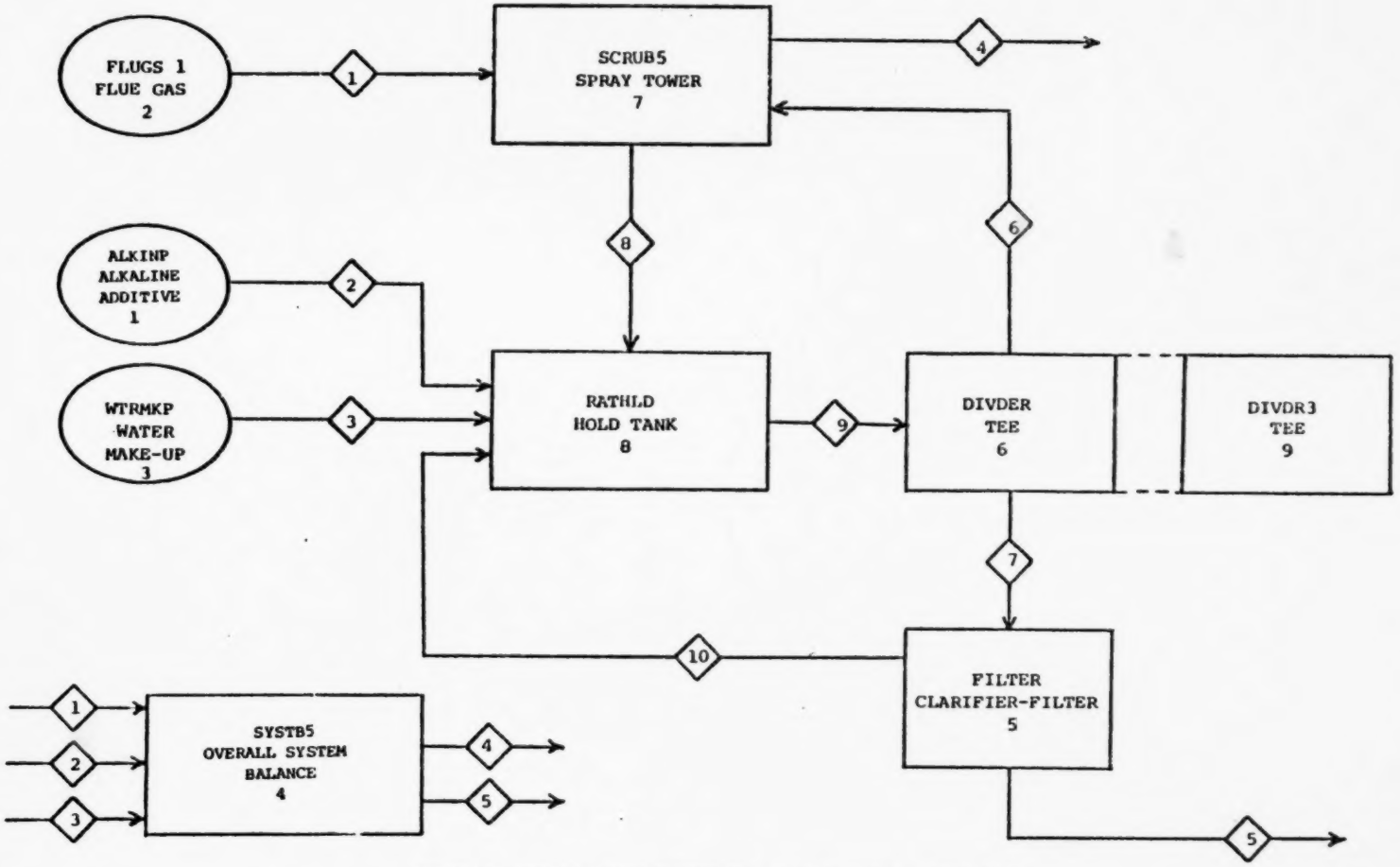

Figure A-1. Process model block diagram.

8) The hold tank closely approaches an idealized backmixed vessel.

9) Neither chemical change nor phase separation occurs to a process stream except in a process unit.

The two assumptions involving the temperature of the process liquor streams should be good approximations. Previous pilot unit work indicates that the scrubber effluent liquor streams closely approach the adiabatic saturation temperature. In simulation cases previously conducted, the water make-up stream was on the order of 0.5 percent of the scrubber feed stream and thus would have a negligible effect upon changing the process liquor temperature. Heat loss to the surroundings should be small in most instances. Assumption three is a good approximation for a short-residence-time contactor with a high liquid-to-gas ratio such as a spray tower. Assumption seven listed above is probably not a good assumption in that it does not reflect the true situation in a clarifier. This modeling assumption may be justified from the standpoint that solid-liquid equilibrium represents the maximum chemical change that can occur across the clarifier. Thus, the actual composition of the clarifier effluent streams will lie between the composition of the clarifier feed and the effluent composition as determined by solid-liquid equilibrium. In general, this chemical change will be small.

EQUIPMENT SUBROUTINES

This section gives a brief description of the major routines used in the process simulations. The routines may be grouped into four sections: (1) input routines (FLUGS1, ALKINP, and WTRMKP), (2) unit operation routines (SCRUB5, RATHLD), (3) material balance routines (SYSTB5), and (4) minor process unit routines (DIVDER, DIVDR3, and FILTER).

FLUGS1

This routine simulates a flue gas input stream with entrained fly ash. It reads data cards for the temperature, pressure, and flow rate of the gas stream and the weight rate of the fly ash, as well as the mole fraction composition of the gas and the weight fraction composition of the solid. The calculations performed are to convert these data to program units and assign them to the specified stream.

ALKINP

This routine simulates an alkaline input stream. It reads data cards for the mass flow rate and weight fraction composition of the additive. The calculations performed are to convert these data to program units and assign them to the specified stream.

WTRMKP

This routine simulates a water input stream. It reads data cards for the weight composition of the water stream and converts these data to molality in the specified output stream. This routine does not assign the flow rate of the output stream.

SCRUB5

This routine simulates a vapor-liquid contactor. It is assumed that (1) the scrubber is adiabatic, (2) CO_2 and H_2O are in vapor-liquid equilibrium, and (3) no precipitation occurs. The flue gas flow rate, composition, and amount of SO_2 removal required is input to this routine. A fraction of the incoming fly ash and certain slurry solids can also be specified to dissolve.

The routine calculates the number of transfer units (and thus $K_g aV$) required to achieve the specified SO_2 removal using the specified feed rate and composition. The composition, scale potential, and SO_2 sorption capacity of the outlet slurry are also calculated. These parameters allow prediction of the required liquid-to-gas ratio to achieve the desired SO_2 removal without scaling in the scrubber.

RATHLD

This routine simulates a well-mixed holding tank. All input streams must be completely known along with the tank volume and the rate constants for the solid-liquid mass transfer of the additive, $CaSO_4 \cdot 2H_2O$, and $CaSO_3/SO_4$ coprecipitate. The output stream is calculated by simultaneous solution of rate, material balance, and equilibrium relationships.

Hold tank performance can be modified by adjusting the tank volume, the slurry solids concentration, or by changing the precipitation and dissolution rate constants. In normal design situations, the tank volume is adjusted so that scaling is prevented.

SYSTB5

This routine performs a mass and energy balance about the process based on complete knowledge of the flue gas and additive streams, the composition of the make-up water stream, and the following system parameters: (1) the fraction of the SO_2 in the flue gas which is absorbed, (2) the fraction of the absorbed SO_2 which is oxidized to sulfate, (3) the pressure drop across the scrubber, (4) the particulate removal efficiency of the scrubber, and (5) the weight fraction solids in the solid waste product. Additional information is taken from other routines as needed. Several options are available for calculating an initial guess for the amount of CO_2 desorbed from the liquor in the scrubber.

Based on total removal of HCl, the specified fractional removal of SO_2, and an initial guess at the loss of CO_2, the non-aqueous portion of the scrubber exit gas is calculated. An adiabatic heat and material balance is then performed to find the water in the scrubber exit gas, assuming that the liquid circulating through the scrubber and the exit gas are both at the adiabatic saturation temperature.

Based on (1) the weight fraction solids in the filter bottoms; (2) complete information for the flue gas, scrubber exit gas, and additive streams; and (3) the composition of the make-up water streams, the filter bottoms flow rate and composition, and the make-up water flow rate are calculated.

DIVDER

This routine simulates a stream splitter. Based on the flow rate for the first output stream and complete information about the second output stream, complete information for the input stream and the first output stream are calculated.

DIVDR3

This routine also simulates a stream splitter. The difference from DIVDER is that in DIVDR3 the feed stream is completely known and the flow rate of the first output stream is known. Based on these data, complete information for both output streams is calculated.

FILTER

This routine models a solid-liquid separator. Input data are the weight fraction solids in the feed and bottoms streams and the separation efficiency, i.e., the fraction of the feed solids which are transferred to the bottoms.

CALCULATION SEQUENCE

In the execution of a simulation computer run, the executive system coordinates the sequence of calculations. First, the data cards are read, the input data are printed, and any necessary initialization (such as assigning the weight fraction solids in the filter bottoms in the FILTER routine) is performed. Secondly, the simulation calculations are performed as directed by the input order of calculations. For the example flow scheme, these calculations are performed in the following sequence:

1) The input routines FLUGS1, ALKINP, and WTRMKP are called. These routines perform all of their operations on the first pass and do not play an active part on subsequent passes.

2) Subroutine SYSTB5 calculates the scrubber exit gas and the filter bottoms stream flows and compositions.

3) Subroutine FILTER calculates the filter feed and filter overhead flows and compositions.

4) Subroutine DIVDER calculates a first guess at the scrubber slurry feed stream and hold tank effluent compositions as having equilibrium compositions.

5) Subroutine SCRUB5 calculates the scrubber bottoms stream based on the level of species absorbed/desorbed in the scrubber, solids dissolution, and water evaporation.

6) Subroutine RATHLD calculates the tank effluent composition based on rate calculations.

7) Subroutine DIVDR3 recalculates the scrubber feed (slurry recycle) and filter feed streams based on the calculated hold tank effluent flow and composition.

8) Steps 5, 6, and 7 (subroutines SCRUB5, RATHLD, and DIVDR3) are iterated until the compositions and flow rates of the streams involved approach their steady-state values.

At this point, the executive system prints complete stream data for all process streams, and the simulation is completed.